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**A FEASIBILITY STUDY FOR THE CONTINUOUS  
AUTOMATED ANALYSIS AND CONTROL OF  
PHOSPHATIZING BATHS**



**TECHNICAL REPORT**

February 1972

RESEARCH DIRECTORATE

WEAPONS LABORATORY AT ROCK ISLAND

RESEARCH, DEVELOPMENT AND ENGINEERING DIRECTORATE

U. S. ARMY WEAPONS COMMAND

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## FOREWORD

This report was prepared by E. P. Perry and R. L. Myers of the North American Rockwell Science Center, Thousand Oaks, California, in compliance with Contract DAAF01-72-C-0130 under the direction of the Research Directorate, Weapons Laboratory at Rock Island, U. S. Army Weapons Command, with S. L. Eisler as Project Engineer.

This work was authorized as part of the Manufacturing Methods and Technology Program of the U. S. Army Materiel Command and was administered by the U. S. Army Production Equipment Agency.

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## ABSTRACT

The feasibility of automating production phosphate coating process baths has been studied under the guidance of the Research Directorate of the Weapons Laboratory at Rock Island. The study comprised a detailed examination of the analysis and control requirements. Continuous automated analysis and control of phosphate baths are feasible. Analytical methods, sampling system procedures, and control logic techniques are presented for incorporation into a prototype system.

## 1. Introduction and Scope of Work

It is the purpose of this study to investigate the feasibility of continuous automated analysis and control of phosphatizing baths. The scope of this report is to define the major problems which would be encountered in constructing such a system, recommend approaches to the solution of these problems and provide a general plan for the implementation of automated control.

The application of corrosion resistant coating is an important phase of the metal finishing industry. Many techniques have been developed to achieve this goal. In general, these techniques are based on a chemical or electrochemical modification of the metal surface. One specific process which provides excellent corrosion resistant coatings is the phosphate coating process. This process was developed in the early 1900's (1,2,3). However, the coatings produced by the early procedures were difficult to obtain and did not satisfactorily withstand severe environments. Empirical refinements in the technique were made and by World War II satisfactory coating was being routinely applied. In the late 1940's and 1950's, the empirical relationships were defined and studied qualitatively (4,5,6,7). As a result of these studies, the optimum concentration for the chemicals in the phosphating baths were known.

The problem of maintaining optimum phosphate bath activity, however, still remains. As yet, no control system has been built which automatically controls all of the important bath variables. The lack of continuous control of bath composition causes a severe problem, since coatings are then produced which do not meet corrosion resistance tests, e.g., salt spray. The production of poor coating causes a loss in material and in the manhours required to rework the failures.

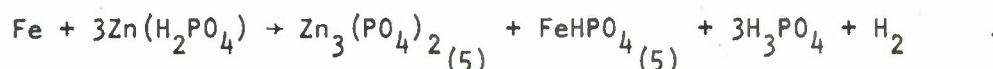


## 11. Introduction to the Phosphating Process

As a prerequisite to automating any process, the process must first be understood as it is performed manually. The phosphating process is no exception. This section of this report will briefly examine the mechanism of the phosphating process, the composition of the phosphate baths and the present method of composition control.

### A. Mechanism of Coating Process

A piece of ferrous material which is to be phosphate coated is first sandblasted, degreased and/or pickled to prepare a fresh clean surface for the protective coating. The material is then immersed in the phosphating bath. In the first step of the process, the iron surface is attacked by the acid. This generates hydrogen gas and ferrous (Fe(II)) ions. The bulk acid concentration must be maintained so that local depletion of the hydrogen ion at the metal surface will be sufficient to effect the precipitation of the metal phosphates on the metal surface. The overall reaction which occurs is given by



If manganese is present instead of zinc, both the secondary and ternary manganous phosphates will be formed. The resulting protective coating is a mixture of ferrous hydrogen phosphate and ternary zinc (or manganese) phosphate. The ratio of the salts present on the surface is dependent upon the ratios of their concentrations of the ions in the plating solution. Most often nitrate will also be present in the baths. The nitrate in the bath acts as an accelerator to speed up the coating process primarily by oxidizing the hydrogen. Further details of the mechanism are not important here, but can be found in a study by Gilbert (7).

### B. Composition of Phosphate Baths

Research conducted on the composition of phosphating solution has shown that there exist optimum concentrations which achieve the maximum corrosion

resistance of the coating while minimizing the time required and the material consumed. As stated in Rock Island Arsenal Report 54-2906, the bath compositions should be (in order of decreasing importance):

A. Zinc Base Phosphating Solution

Free Acidity	4.0 points maximum*
Total Acid	24-27 points*
Free to Total Acid Ratio	Not lower than 1-6.0
Iron (Ferrous)	.40 to .50%
Nitrate	2.0 to 2.5%
Zinc	.15% to equal the percent iron
Total Metal	Not lower than .50%
Zinc to Iron Ratio	1-1 to 1-1.5

B. Manganese Phosphating Solution

Free Acid	1.3 to 4.0 points*
Total Acid	24-27 points*
Free to Total Acid Ratio	1-6.0 min. (1-6.5 preferable)
Iron (Ferrous)	.20 to .40% (.30% preferable)
Manganese	.20 to .50%
Total Metal	.40 to 1.0%
Manganese to Iron Ratio	1-1 to 1-1.5
Nitrate	.3 to 1.0%

\*One point equals 1 ml of 0.1 NaOH per 10cc sample.

From the above specifications it is clear that the acid and iron concentrations are the most important. Although it is not explicitly stated in the specifications, the difference between the total acid value and the free acid value is a function of the amount of phosphate present in the solution.

C. Control of Bath Composition

Even though the optimum concentrations of the bath have been known for sometime, a completely satisfactory procedure for controlling the composition of the bath to meet the optimum values has not yet been developed. Presently, a sample is withdrawn from the bath and analyzed using wet chemical techniques. If the analyses show that one or more constituents do not fall within the tolerance range, chemicals must then be added to correct the composition.



The type and amount of chemical to be added is calculated from predetermined tables. A typical table is shown here as Table 1. This particular table is for the zinc phosphate solution and was taken from Rock Island Arsenal Report 54-2906. Immediately the complexity of the control is apparent. To correct a given deficiency, the proper amount of one or more of five chemicals must be added. For example, assume that the results of the analysis are:

Free acid	2.0 points
Total acid	23 points
Ferrous	.42%
Zinc	.05%
Nitrate	2.2 %

Comparing these values to the optimum range quoted in the previous section, one finds that: 1) the free acid is under its maximum values; 2) total acid is less than the minimum permissible; 3) ferrous is within optimum range; 4) zinc content is low; and 5) nitrate is within optimum range. It is, therefore, necessary to select a control chemical from Table 1 which causes total acid and zinc to increase while not changing free acid, iron and nitrate. The closest response which can be found is that for the modified replenisher. It is noticed, however, that the addition of modified replenisher will also increase the free acid concentration. The free acid is below its maximum allowed value so a slight increase will be tolerable. Thus, modified replenisher would be added to increase the total acid to the middle of the optimum range. The addition of replenisher would hopefully correct the zinc value and not change the free acid significantly. If, however, analysis after the addition showed the same or other deficiencies, a similar decision and addition process would be necessary.

From the above discussion, it can be concluded that the primary problems of automatic control of phosphate baths are the analysis of solutions and the complex problem of reagent addition. This study will concentrate on these two areas and also include discussion of the lesser problems which are more easily solved, but nonetheless still important to the successful operation of the system.

Table 1. Control Measures for Zinc Base Phosphating Solution

Additions	Free Acid	Total Acid	Iron Content	Zinc Content	Nitrate Content	Note
Phosphoric Acid	Increases	Increases (slight)	Same	Same	Same	1
Iron Syrup & Zinc Oxide	Increases	Increases	Increases	Increases (slight)	Same	2
Modified Replenisher	Increases	Increases	Same	Increases	Same (approx.)	3
Basic Zinc Nitrate	Decreases	Increases	Same	Increases	Increases	4
Iron Chips-Steel Wool	Decreases	Decreases	Increases	Decreases	Decreases	5
Iron Syrup, No Zinc Oxide	Increases	Increases	Increases	Decreases (slight)	Same	6

- NOTE: 1. Add in small amounts only.
2. 1 gal/100 raises iron approx. 0.01%.
3. Add only enough to raise total acid to normal.
4. (1 gal 36 Be) mixture raises nitrate/100 -- .65%.
5. Use when free acid is high and iron percent is low.
6. Zinc Oxide is added to hold free acid down.



### III. Introduction to Automatic Process Control

Encompassed in the area of most automatic process control systems are the disciplines of chemistry, chemical engineering, mechanical engineering, electrical engineering and computer sciences. A properly designed system will incorporate the knowledge and techniques of each of these fields in order to achieve optimum results.

#### A. Advantages of Automatic Process Control

A principal advantage of automatic control is that of improved precision of control. This results in a more uniform product, reducing the time lost due to producing goods which fail to meet quality standards. A second feature is that of constant supervision. The operator is then able to perform other useful functions and the process is less subject to fluctuation caused by operator mental lapses which so often occur when a human is subjected to a repetitive, uninteresting task.

The principal disadvantage of automatic process control is the time and expense required for implementation. As will be considered later in this study, considerable work must be expended in order to consider every detail of the operation.

#### B. Basic Elements of the Control System

The basic elements of any process control instrumentation are the sensor, the comparator and the corrector (Figure 1). A simple example of this mechanism is the temperature control of a heated bath. The sensor can be a thermistor or bimetallic spring. The set point can be set to a resistance or spring position corresponding to a particular temperature. Should the temperature fall below the set value, a contact could close signifying the results of the comparison. The closed contacts could then be used to correct the temperature by turning on an electric heater or actuating a steam valve.

The preceding example was a very simple one. Only one variable was controlled and the control function was implemented with analog signals with the resultant action being on or off. The extension of process control to more complex systems requires considerably more elaborate equipment. This is

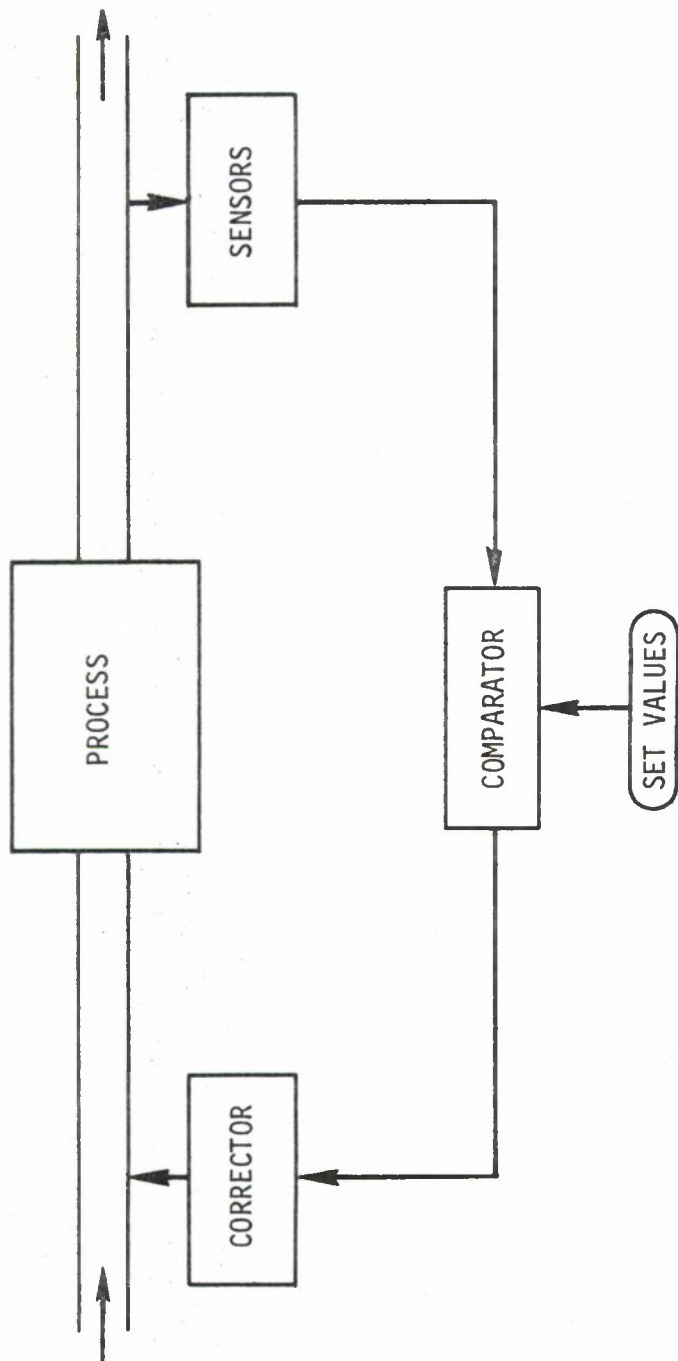


Figure 1 - Process Control Loop



especially true of situations where most or all of the variables are inter-related. The advent of the small or mini-computer has made economically feasible many process control applications which were previously too complex for automatic schemes. The power of the mini-computer in these applications is four-fold. First, the computer can perform computations very quickly. Second, the ability to make decisions is an integral part of the computer. Third, the computer can be interfaced to external devices so that they can be controlled by the computer. Fourth, the computer is easily reprogrammed to accommodate any modification which may be desired for the process. These changes are very difficult and expensive to make in a hardwired controller.

Using the mini-computer, three different possible configurations are presented (Figures 2, 3 and 4). In each case it is assumed that the computer has been preprogrammed to analyze the data and to perform the decision making process. In the first, the computer acts independently in its decision making role (Figure 2). This is an open control loop, since operator interaction is necessary. The operator must input to the computer the readings from the sensors. The computer will then output the proper control actions to be taken and it is left to the operator to actually execute these functions. The second approach (Figure 3) is to have the computer control the analysis, read the data directly and perform the necessary calculations. Since the operator must perform the actual corrections necessary, the control loop is still open. The final approach (Figure 4) represents fully automatic control. The control loop has been closed excluding the human operator. The computer controls the analysis, reads the data, makes the decisions and controls the reagent addition. The human operator is needed only for routine maintenance or the remote possibility of system failure.

Since the phosphate process is quite complex, the remainder of the discussion will tacitly assume that a mini-computer will be included in the final configuration. The specification of continuous automated analysis and control requires that the computer assume a role as shown in Figure 4. The remainder of this study will develop in detail the specific interactions which will be required.

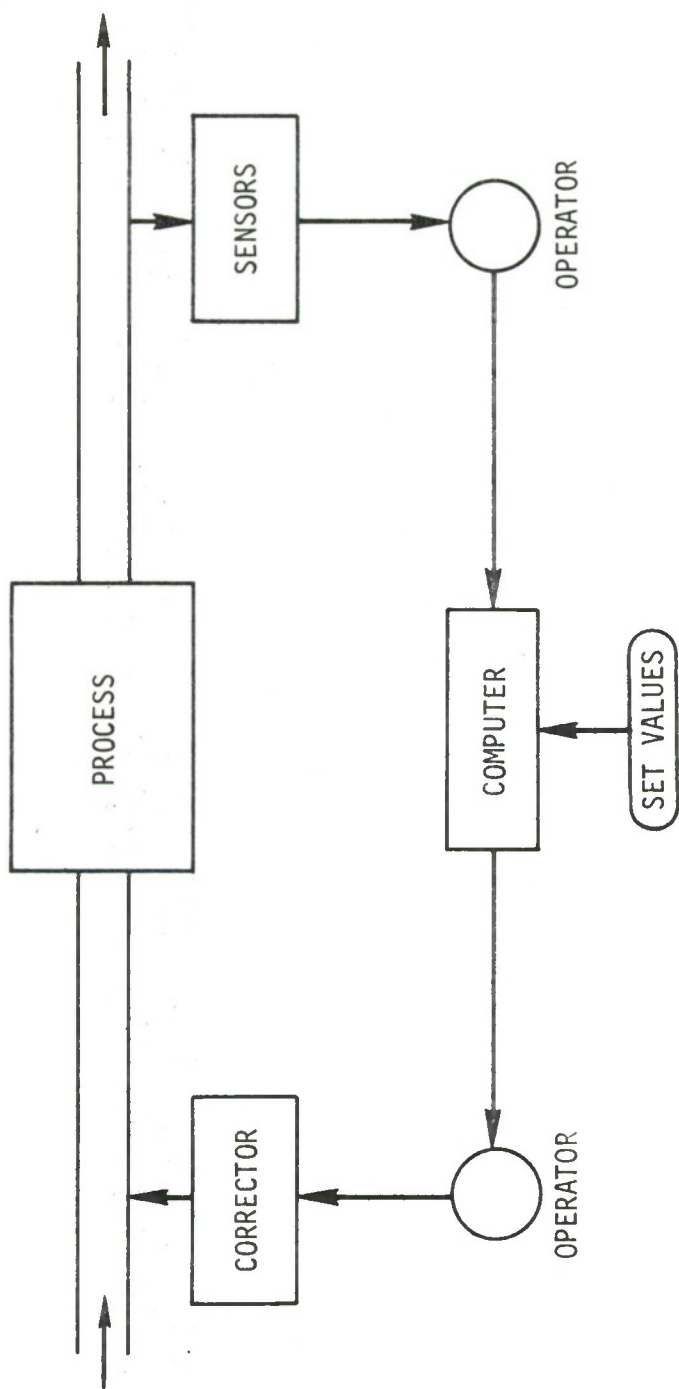


Figure 2 - Computer Function as a Comparator in Process Control



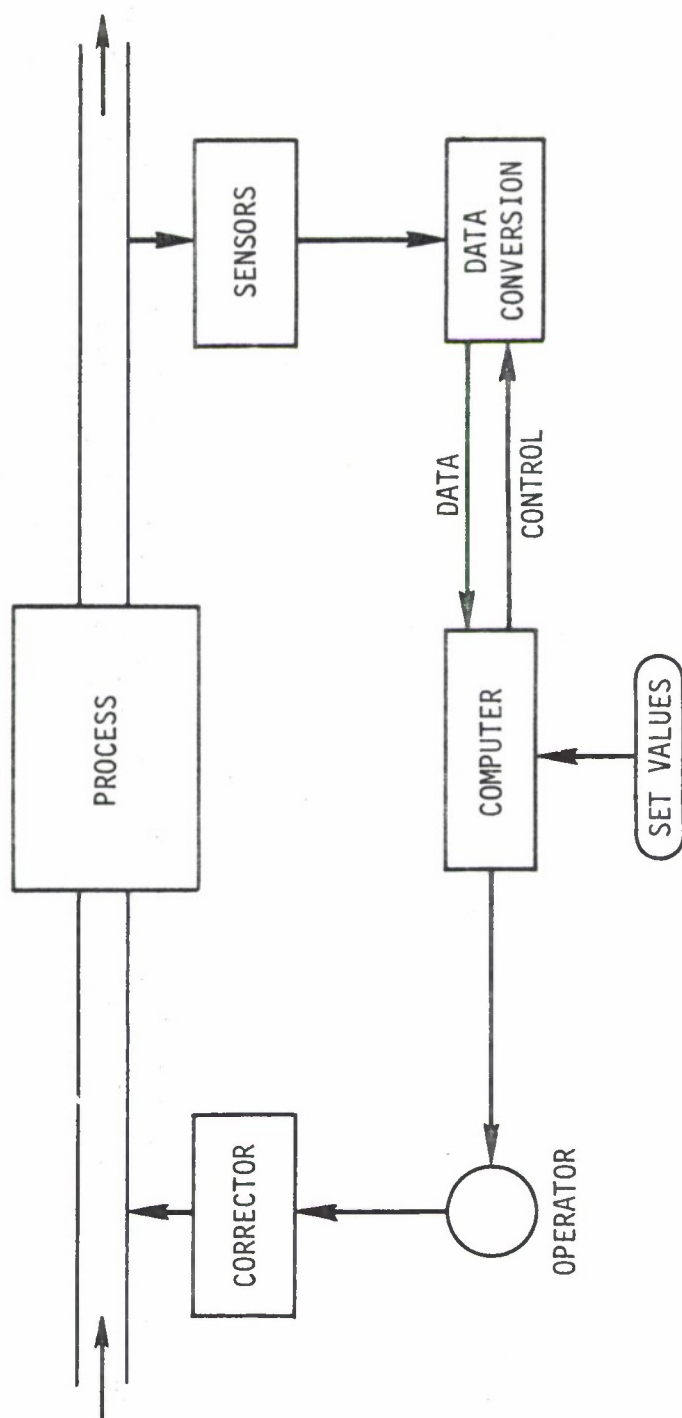


Figure 3 - Computer Automated Analysis in Process Control

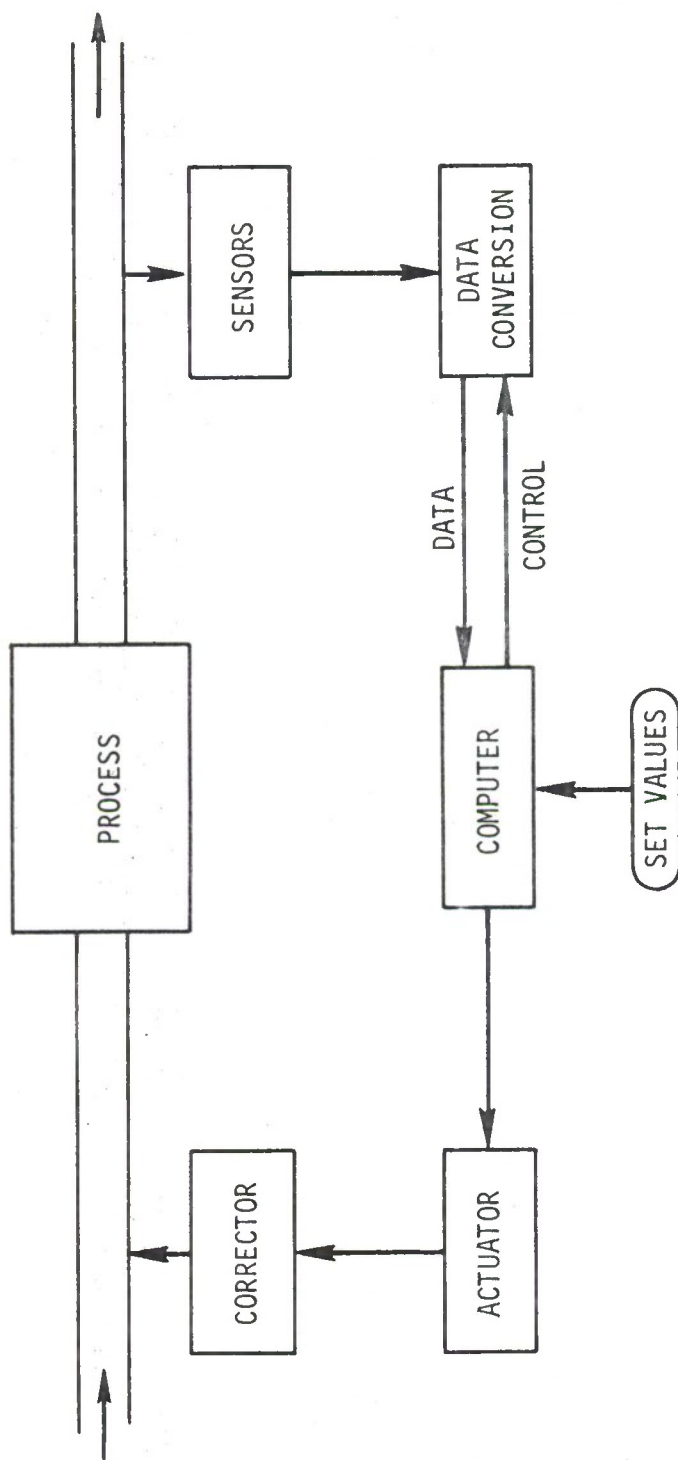


Figure 4 - Computer Automated Closed Loop Process Control

### C. Design of a Data Acquisition System

The basic relationship of the computer to analytical instruments has been described in the previous section. Communication between the devices is bidirectional. First the computer sends control signals to the instrument directing it and perhaps assisting in making the analysis. During or at the conclusion of the analysis the analytical instrument sends data to the computer. The necessity of communication between the computer and the rest of the system imposes the stringent restriction that all information must be in the form of electrical signals (digital or analog). In terms of this analysis, the restriction means that titration end points must be transduced to electrical signals. For example, the computer and analog to digital converter alone cannot detect the color change of an indicator. If a color change were to be detected, a spectrophotometer would be necessary to provide an electrical signal proportional to the intensity of light at a given wavelength. In terms of sampling and analysis, the restriction means that all valves must be ultimately controlled by electrical command whether directly (solenoid valves) or indirectly (motor-controlled pneumatic valves).

A more detailed description of the interaction is shown in Figure 5. In this example, the computer is selecting one of three process streams to be analyzed. This is implemented by a series of solenoid actuated valves. The selected stream is directed to the analytical instrumentation. This instrumentation may be passive in the sense the computer need only to sample the data and not control the experiment. Examples would be a thermocouple or a pH reading. However, for the majority of analyses, the computer must take a more active role. A typical example of this type is an automatic titrator. This device must be sequenced by the computer, a chore most normally performed by the human operator. First, the buret must be filled and the sample must be moved to the analysis cell. Next the start of the titration must be synchronized with the start of the data acquisition so that the data points of the titration curve accurately correspond to the volume of titrant added. Finally, the computer must stop the titration after the end point and purge the analysis cell. All of these small steps in the analysis, which the human operator performs as a matter of routine, must be designed into the computer interface in



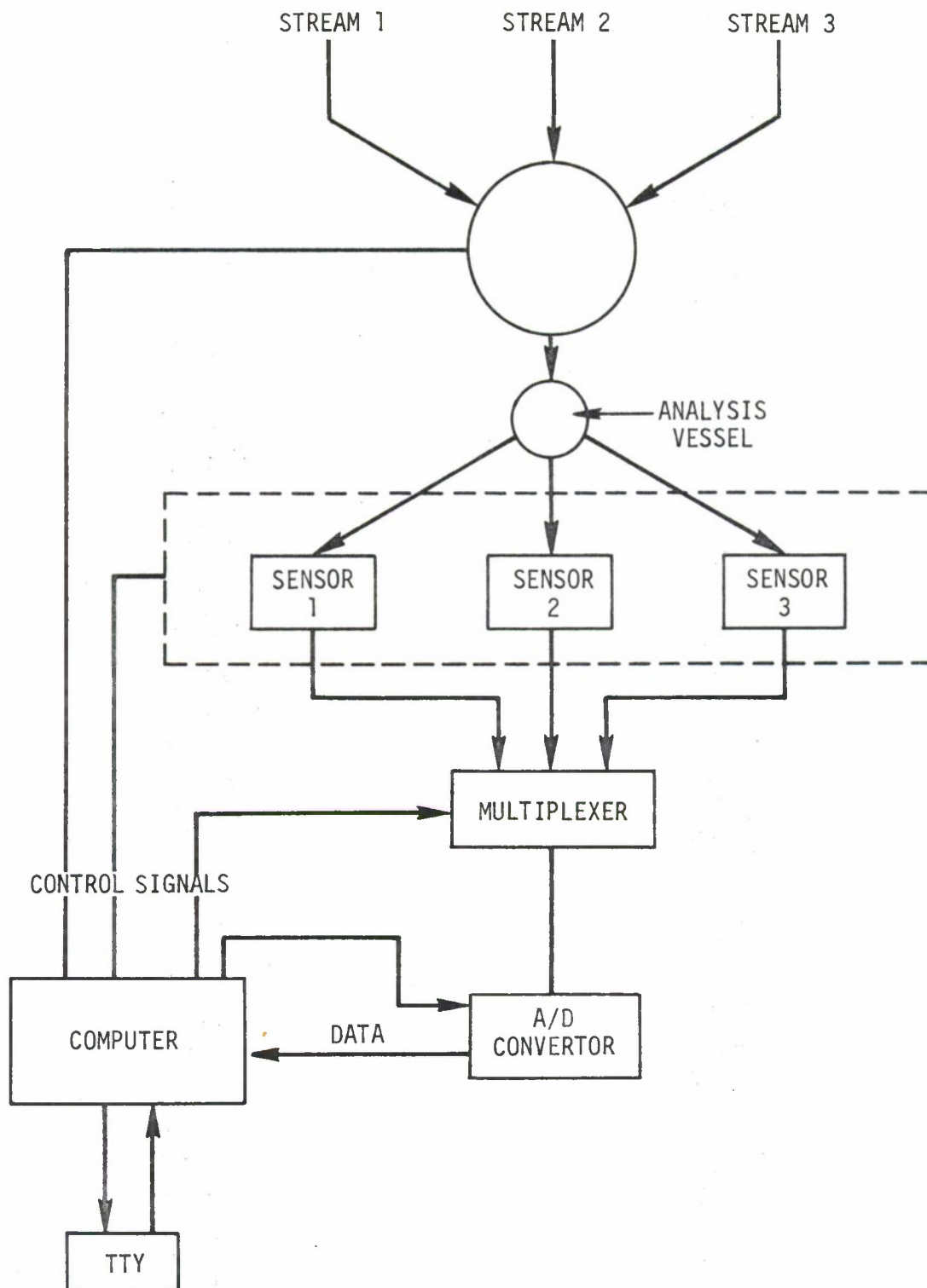


Figure 5 - Block Diagram of Automated Analysis System

order to achieve a fully automated analysis.

In a manner similar to the selection of the process stream to be analyzed, the computer must also decide which of the signals from the analytical instruments are to be converted to digital data at what points in time. The device which accomplishes this goal is known as a multiplexer. The multiplexer is generally designed so that any one of the channels can be selected at random or the channels will be sequentially selected upon receiving an advance command. The order and frequency in which the computer accesses each channel will, of course, depend on the experiment being performed.

In order that the signals from the instruments be of any use to the computer, they must be converted to digital format. This is the function of the analog to digital converter. Analog to digital converters are available in a multitude of configurations. The options include: conversion time, e.g., from less than  $1\mu\text{sec}$  to 1 sec; accuracy and precision, e.g., from  $\pm 25\%$  to  $0.01\%$ ; and full scale ranges, e.g.,  $> 1 \text{ KV}$  to  $< 10\text{mV}$ . Selection of a particular converter will also be based on the needs of the system. A conversion technique which is particularly useful in slower applications (conversion time  $> 1 \text{ msec}$ ) is the use of an autoranging digital voltmeter. In order to display digital numbers, an analog to digital conversion must be performed. The coded outputs of the voltmeter are generally available for external devices such as printers or computers. Autoranging digital voltmeters are particularly convenient since they can typically convert analog signals over a range of 1 KV to  $1\text{mV}$  at  $0.01\%$  accuracy with a lower limit of  $1\mu\text{V}$ .

The data from the analog to digital converter is transferred to the computer upon command of the computer. At this point, the data is available for calculations. Further information can be obtained from the operator through the teletype. Status and action messages are also sent via the teletype to the operator.

The extension to automatic closed loop control is easily accomplished from this point. It is only required that the computer control the corrective addition procedure through the use of pumps and valves similar to those used for the sampling system.

#### D. System Expansion

One of the advantages of developing an automatic process control system for phosphating baths which involves a mini-computer is the capability of extension of the control to more than one bath. The rate at which phosphate baths need to be monitored is anticipated to be very slow compared to the speed of the computer and analysis system. Once the system is developed, it would be a straightforward project to extend the sampling system to sample more than one solution. It would similarly be a straightforward, but more complex procedure, to extend the computer programs to control more than one bath. The point of emphasis is that only one computer system would be necessary. Thus, the majority of both development and hardware costs are eliminated in extending control to several baths.



#### IV. SELECTION OF ANALYTICAL SCHEME

This section describes the different methods of analysis which were considered to determine those most suitable for automation of the phosphate baths. The methods were evaluated by comparing estimates of simplicity, reliability and precision.

##### A. Current Methods of Phosphate Bath Analysis

For control of the phosphating baths, analyses for free and total acid, nitrate ion, ferrous ion, manganese(II) ion (for manganese bath) and zinc(II) ion (for zinc bath) are desirable. The present analytical scheme, as described in Rock Island Arsenal Report 54-2906, involves a titration with base using two different indicators to obtain free and total acid. Ferrous ion is determined by direct titration with potassium permanganate using the permanganate color as the indicator. Nitrate ion is determined by a somewhat complex redox method, while manganese is determined by oxidation to permanganate followed by titration with ferrous ion. Zinc is determined by a precipitation titration with ferrocyanide. The most important of these analyses for bath control appears to be the analysis for free and total acid and ferrous ions.

If modified, some of these currently used techniques serve as a basis for an automated analytical system. For example, a titration for free and total acid with potentiometric end point detection and a direct potentiometric titration for ferrous ion with potassium dichromate as the titrant would provide quite satisfactory automated techniques. The procedures currently used for nitrate ion, zinc ion and manganese ion, are somewhat complicated, involving a number of steps, requiring the addition of solid reagents and heating. Thus, they do not appear to be suited for automation.

##### B. Manganese and Zinc Bath Analyses

###### 1. Free and Total Acid

As indicated above, a titration with base using two indicators, methyl orange - xylene cyanole mixed indicator and phenolphthalein, is now used to determine the free and total acids. In the usual definition, free acid constitutes the concentration of uncombined but hydrated hydrogen ions, while

total acid constitutes the sum of the uncombined and combined hydrogen ion concentrations (as in weak acids). While the former could be measured directly using a hydrogen ion (pH) electrode (activity is actually measured but concentration can be derived if conditions are sufficiently defined), the only way to obtain the latter is through titration with base. As long as titration is required to obtain the total acid, it is no more difficult to obtain both free and total acid by titration and generally much more accurate. Thus, potentiometric titration appears to be the superior technique to obtain these values.

For the manganese phosphate solution, the potentiometric breaks are not very well defined. Figure 6 shows a titration for a 10 ml sample which was obtained from Rock Island on the 12th of November. This curve is similar to those shown by Gilbert (4). Since the samples were somewhat aged and not heated, the quantitative results of titration are not too meaningful. The shape of the titration curve may also have been affected, but probably not significantly. Of particular interest is the pH range for the color changes of the two indicators in Figure 6. These indicator changes, particularly the second, do not coincide with the analytical (potentiometric) end point. It would thus seem appropriate to titrate to a given pH value. For the manganese bath, the free acid range is from 1.3 to 4.0 points (mls.) while the total acid has an acceptable range from 24 to 27 points (mls.). Because of the approximate 3 point range which defines the working concentration for both free and total acid, an uncertainty of approximately 0.5 ml would seem to be satisfactory, and uncertainties significantly less than this should be possible if a titration is done to a given pH value (see curve).

For the zinc phosphate solution, the titration curve is somewhat better defined (Figure 7) but, as with the previous solution, the indicator does not change color at the break point of the titration. Thus, titration to given pH values is preferable here also. The uncertainty of end point detection would appear to allow adequate control capability, since the free and total acid concentration ranges are about the same as for the manganese phosphate solution. Potentiometric titrations have been shown to be quite readily automated as described in the next section.

## 2. Nitrate Ion

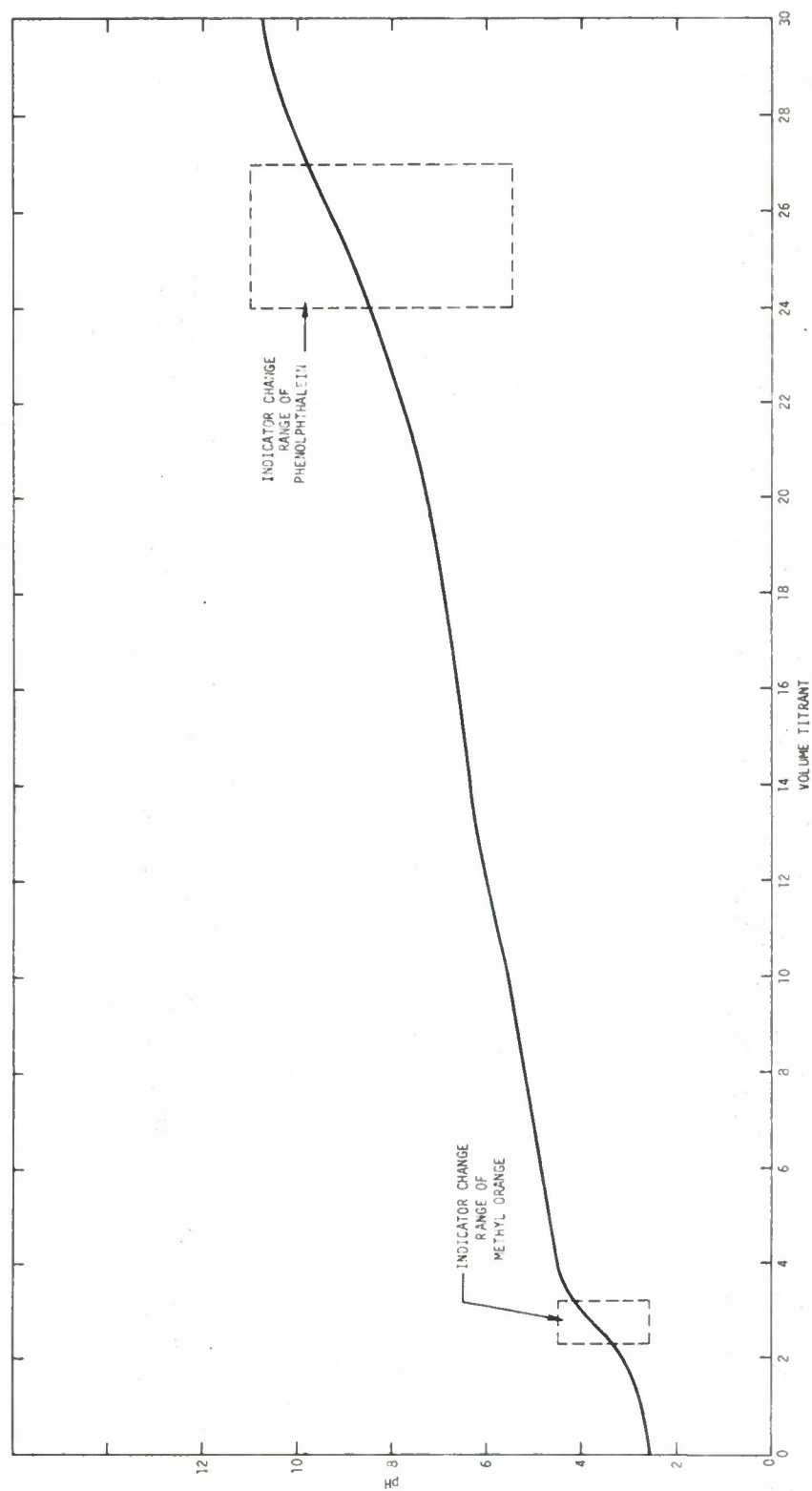


Figure 6 - pH Titration Curve for Mn Phosphate Solution



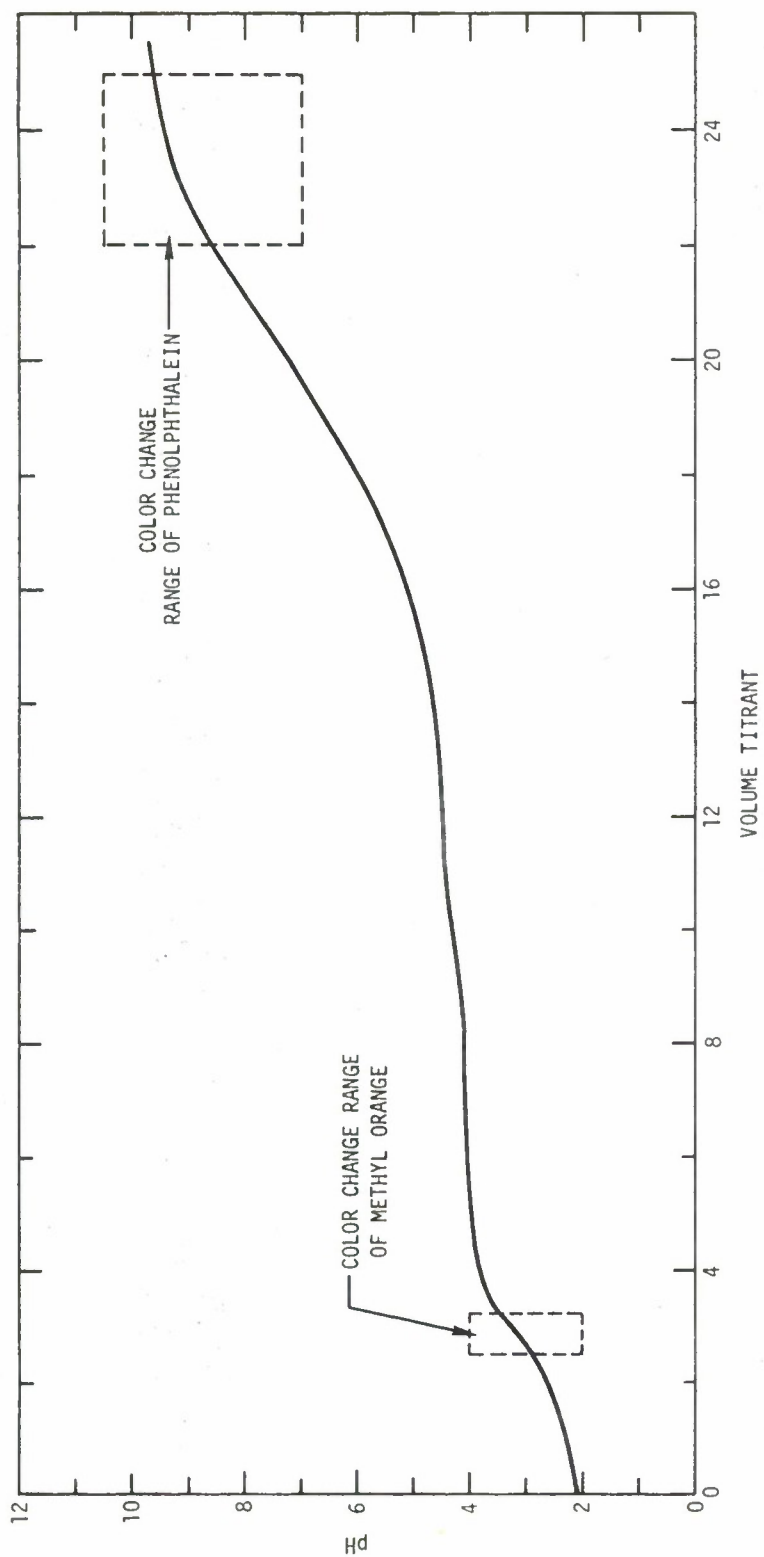


Figure 7 - pH Titration Curve for Zn Phosphate Solution

Highly selective nitrate ion electrodes are commercially available (8) for the determination of nitrate ion in the presence of other cations and anions. One of these electrodes was tested for the determination of nitrate in the phosphating baths. The potential of this electrode responds to the activity of the nitrate ion according to the relation

$$\pi = \pi^{\circ} + K \ln a_{\text{NO}_3} \quad [1]$$

where  $\pi^{\circ}$  is a reference potential and  $K$  is a constant. If the electrode responds such that  $K$  is equal to  $RT/nF$ , then the electrode response is Nernstian. If Nernstian behavior is assumed, differentiation of equation [1] gives the expression

$$\Delta\pi = \frac{0.06}{2.3n} \left( \frac{\Delta C}{C} \right) \quad [2]$$

where the activity coefficients are ignored, and  $C$  represents the concentration.

Figure 8 shows a semi-log plot of nitrate ion concentration vs. electrode potential. The slope of this line is 58mV. Since for nitrate ion  $n = 1$  this is close to the Nernstian value. From equation [2] we then calculate that for a 5% change in concentration, the potential will change by 1.3 millivolts. In actual fact, it is a 5% change in activity, not concentration, so if the ionic strength of the medium changes, the potential change will be somewhat different from this. Figure 9 shows a plot of  $\Delta\pi$  in millivolts vs.  $(\Delta C/C)$  for data obtained by dilution of a zinc phosphate solution. Equation [2] indicates that the slope of this plot should be 26 millivolts. The actual slope is 27 millivolts. The potential of the electrode is not affected by the presence of phosphate ion. For example, the electrode potential measured in a  $10^{-2}$  M sodium nitrate solution was 51mV. Addition of .01 M sodium dihydrogen phosphate did not change that potential, while addition of 0.1 M sodium dihydrogen phosphate gave a potential value of 50mV. Because of this repeatability, it is felt that the concentration of nitrate in the zinc bath can be measured to  $\pm 5\%$  relative. The concentration range which is acceptable for the nitrate concentration in the zinc bath is from 2.0 to 2.5%, corresponding

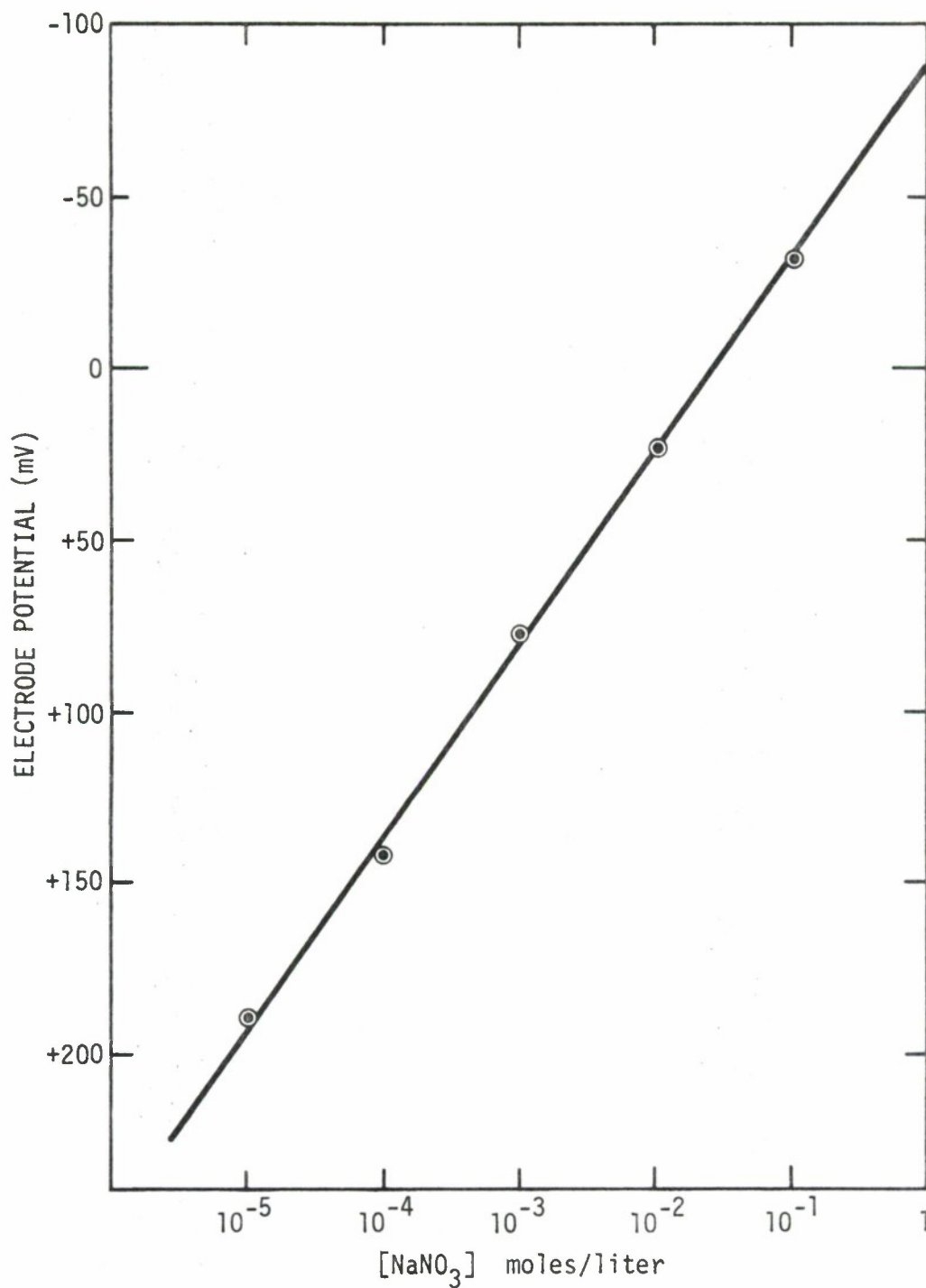


Figure 8 - Response Curve for Orion Nitrate Ion Electrode



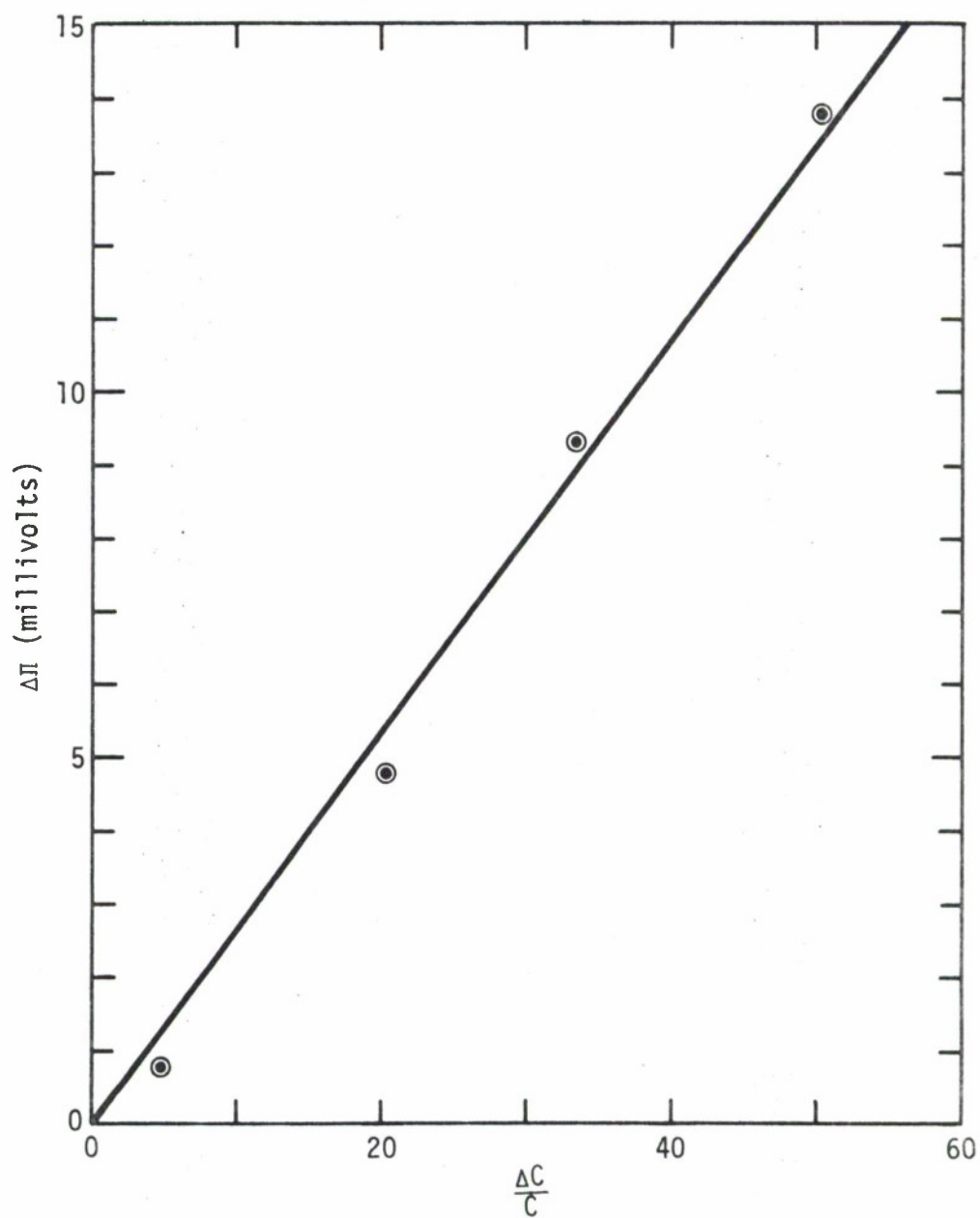


Figure 9 - Plot of  $\Delta C/C$  vs.  $\Delta\pi$  for Nitrate Ion Electrode

to a relative range of 25%. It is felt that this precision is probably sufficient for the measurement. However, some additional testing should be done to back up this preliminary conclusion. The above concentration range corresponds to a molarity range from 0.32 to 0.40 M. Because it is recommended that this electrode not be exposed to high concentrations of nitrate, it may be necessary to dilute the solution 50-fold in order to improve the measurement. In addition, the slope of the potential vs. log concentration plot in this range may be somewhat less because of ionic strength effects (see Figure 9).

In addition, since the activity of the ion is measured, the activity coefficient must remain constant from solution to solution in order to obtain concentration from the calibration plot. It is advantageous that the ionic strength of this bath should not change appreciably for these measurements. This is realizable since the ionic strength is a function only of the total number of ions and their valence present, not on any specific ion.

In addition, the electrode shows some response to the hydrogen ion concentration at these low pH values (9). If the hydrogen ion concentration remains sufficiently constant in the bath so this interference can be corrected for by the calibration curve, or if the response is small, no problem exists. Data to date suggest this to be true; however, this must be evaluated experimentally in more detail. One of the problems noted with this electrode is the instability over longer periods of time. A drift in potential occurs which requires that a calibration technique be added to the electrode operation.

The potential of the nitrate electrode in the manganese plating solution, although in the right potential "ballpark", was found to drift steadily upward with time. The reason for this drift was not determined. Additional studies will be required to explain this drift and to determine if the electrode can be used to measure nitrate in the manganese bath.

### 3. Ferrous Ion

The presently used technique for ferrous ion involves the direct titration with potassium permanganate using the permanganate color as an indicator of the end point. A modification of this approach which would be suitable for automation involves the direct titration of ferrous ion using a potentio-

metric end point. No pretreatment of the sample is required. Potassium dichromate or ceric sulfate would be preferred for the titration since standard solutions of these reagents are highly stable. The titration curve obtained with these reagents has a well defined break and a derivative of the titration curve as obtained by the computer can give a very accurate indication of the end point. The relative precision of this titration for the ferrous ion concentration is expected to be better than 1%.

The concentration range specified for ferrous ion in the zinc bath is from 0.4 to 0.5%. For the manganese bath, it is from 0.20 to 0.30%. These represent relative ranges of approximately 20 and 30%, respectively. Thus, the precision achievable by this titration is more than adequate.

A polarographic technique can be used for the determination of ferrous ion. It has a significant advantage in that either manganese or zinc and ferrous ion can be determined simultaneously (see below). Unfortunately, the precision obtainable with this technique is not as good as the titration. Previous studies have demonstrated that a precision from 3 to 5% could be readily achieved using automated polarographic procedures. This might be improved slightly. Even the poorer precision could still be used, provided a proper analysis frequency and control scheme were used. This will be discussed further in the next subsection. It is obvious that if such an approach were used, the direct titration of iron would not be necessary.

Other techniques could be employed (i.e., colorimetric procedure using ortho phenanthrophthalein) but would not be as precise and would be equally or more difficult to automate because of possible additional sample handling.

#### 4. Manganese Ion

A number of techniques have been used for the determination of manganese (Table 2), but only those which appear to be suitable for automation will be discussed in detail. The various approaches to manganese determination will be discussed individually.

(a) Ion Selective Electrode. A technique which has several advantages (if it is feasible for this determination) is the use of an ion selective electrode. A divalent cation-ion elective electrode is commercially available. With this electrode, therefore, it should be possible to determine

Table 2. Comparison of Methods for Determination of Manganese

Technique	Description of Method	Interferences	Advantages	Disadvantages
1. Titrimetric	Redox titration of Mn after oxidation to $MnO_4^-$ .			Original oxidation of Mn not easily automated (unless $O_3$ is used).
2. Titrimetric	Redox titration of Mn(II) with $MnO_4^-$ in pyrophosphate medium.	Ferrous ion will presumably interfere.	May be able to determine sum of Fe(II) and Mn(II).	
3. Titrimetric	Complexometric titration with EDTA after removing interference of iron species by masking.	Ferrous and ferric ions.		In masking iron, need to add several reagents & heat solution; not easily automated.
4. Colorimetric	Oxidize Mn(II) to $MnO_4^-$ measure color.	Any colored species or ppts.		Same as 1.
5. Colorimetric	Reaction with formaldoxime to give reddish brown product.	Iron interferes.		Use cyanide and ascorbic acid to get rid of interference.
6. Colorimetric	Oxidize Mn(II) to Mn(III) by air in basic triethanol amine to give green complex.	See text.		
7. Polarographic	Measure Mn(II) & Fe(II) in same electrolyte.	Not know yet. Fe(III) can interfere in pulse polarographic method.	Can measure both ions simultaneously.	May need to use dropping mercury electrode.
8. Ion Selective Electrode (possible only)	Measure potential of electrode which may be related to sum of ferrous ion and manganese ion.	Not known.	Probe is simple to use & inexpensive.	Problems involved in precise enough measurements; may need frequent calibration; needs constant ionic strength solutions.



the sum of ferrous and manganese(II) cations. No experimental work has been done with this electrode as a part of this study. Such work is required to determine its ultimate suitability for this analysis. As with the nitrate electrode, the potential of the electrode is determined by the activity of the cations involved. Thus, the same factors as evaluated for the nitrate electrode are important for this experimental program. Such things as ionic strength effects, uncertainty of potential measurement with subsequent uncertainty in concentration and nature of electrode response with concentration will need to be determined. In addition, the selectivity of the electrode to manganese(II) ion compared to ferrous ion will have to be determined. With suitable electrode calibration, the concentration of manganese could probably be determined directly to  $\pm 5\%$ . This might be adequate for control purposes but greater accuracy would be better.

However, the real potential of the divalent cation electrode is not realized in a direct potential determination. A significant advantage is gained by using the electrode to detect the end points of complexometric titrations. The divalent cation electrode is not sensitive to EDTA complexes since they do not have a charge of +2. Thus, although the potential error of direct measurement may be several millivolts (corresponding to 5-10% change in concentration), this error is insignificant compared to the normal potential change of several hundred millivolts at the end point of the titration (corresponding to a typical change of concentration equal to 5 or 6 orders of magnitude). For this reason, the best results will probably be obtained by using the divalent cation electrode for end point detection.

(b) Polarography. While manganese is not the ideal ion for polarographic determination, it does have some favorable characteristics for determination. One of the main advantages of the polarographic technique is the possibility that both manganese ion and ferrous ion can be determined simultaneously in the same medium, thus simplifying the analysis. Both normal and classical polarography, as well as pulse polarography, should be considered. If significant amounts of ferric ion exist in the bath along with the ferrous ion, a supporting electrolyte for application of pulse polarography needs to be selected in which the ferrous-ferric ion couple is somewhat irreversible.

For normal or classical polarography, a reversible wave can be used, as long as the manganese(II) ion wave is sufficiently separated from the ferrous ion wave. The concentration of ferric ion which can exist in phosphating baths has been determined (10) and has been found to be highly dependent on the nitrate ion concentration and temperature. The greater the nitrate ion concentration, the more soluble is ferric phosphate. In a phosphating bath containing 1% nitrate, the solubility of ferric phosphate is 0.03 g/l at 200°F. This is approximately 1/100 that of the concentration of ferrous ion. At room temperature, the solubility of ferric phosphate is 1.48 gms. per liter in the presence of 1% nitrate. However, if a sample is taken at 200°F and it is separated from all sludge and particulates before cooling, the interference of ferric ion would still be expected to be negligible. The withdrawal of adequate samples from the bath without obtaining sludge in the sampling lines and valves is discussed later. Moreover, it would be expected that the concentration of ferric ion would be maintained reasonably constant under all acceptable bath conditions, because it is determined by the solubility of ferric phosphate. Therefore, the use of an irreversible wave for iron in the application of pulse polarography to the determination of ferrous ion does not seem to be necessary. This needs to be experimentally demonstrated. Table 3 lists possible candidates for the electrolyte choice for simultaneous determination of ferrous and manganese ions in the bath. Inspection of the table indicates that there are several electrolytes which look quite promising for the simultaneous determination of manganese(II) and ferrous ions. The specified range for the concentration of manganese in the phosphating bath is from approximately .04 M to .09 M. By a fifty-fold dilution of this original solution, the concentration would be essentially in the optimum range for polarographic analysis. Because ferrous iron has about the same concentration range, the determination of both ions would appear possible using the same dilution.

Previous studies have indicated that it indeed is possible to use a dropping mercury electrode as an indicator electrode in automated procedure. However, it is probably the most serious drawback of this technique, and techniques are under investigation for replacing this electrode with a solid

Table 3. Possible Electrolytes for Simultaneous Polarographic Determination of Manganese and

Ferrous Ions				
Electrolyte	Electrode Reaction	$E_{1/2}$	Suggested Technique	Suggested Procedure
2F $K_2CO_3$ pH $\sim$ 11	$Mn(II) \rightarrow Mn(III)$	-0.1	Pulse Polarography	Measure $Fe(II) \rightarrow Fe(III)$ at about -0.3. Measure $Mn(II) \rightarrow Mn(III)$ at 0 V.
	$Fe(III) \rightarrow Fe(II)$	-0.53		
	$Fe(III) \rightarrow Fe(II)$	-0.86		
0.25F $Na_2$ Tartrate 2.0F NaOH	$Mn(II) \rightarrow Mn(III)$	-0.46	Normal (or pulse if $Fe(III)$ is very small).	Measure $Fe(II) \rightarrow Fe(III)$ at about -0.7 & $Mn(II) \rightarrow Mn(III)$ at -0.25.
	$Fe(II) \rightleftharpoons Fe(III)$ (rev.)	-1.0		
0.3F Triethanol-amine 0.1F NaOH	$Mn(II) \rightarrow Mn(III)$	-0.5	Normal or pulse.	Same as above.
	$Mn(III) \rightarrow Mn(II)$	(? -0.5)		
	$Fe(II) \rightleftharpoons Fe(III)$ (rev.)	-1.0		
	$Mn(II) \rightarrow Mn^0$			
0.1F $(NH_4)_3$ Citrate pH $\sim$ 6	$Fe(II) \rightarrow Fe(III)$	-0.183	Normal or pulse.	*Measure $Fe(II) \rightarrow Fe(III)$ at 0.0 V. Measure $Mn(II) \rightarrow Mn^0$ at about -1.7 V.
	$Fe(III) \rightarrow Fe(II)$	-0.225		
	$Fe(II) \rightarrow Fe^0$	? not given		
	$Mn(II) \rightarrow Mn^0$	-1.615		

\*Ferrous reduction to the metal may interfere with the manganese wave.

stationary electrode.

(c) Redox Titrations. Perhaps the most common titrimetric method for manganese is the oxidation to permanganate with an oxidizing agent, then titration with either ferrous ion or arsenite. There are, however, problems associated with the employment of the usual oxidizing agents. Thus, common oxidizing agents such as potassium periodate, ammonium persulfate, sodium bismuthate, etc. require a filter step, heating of the solution or some other complication to the sample handling procedure. It has been stated (11) that manganese(II) can be oxidized to manganese(VII) by bubbling with a stream of oxygen containing 5% ozone. The excess ozone is removed by bubbling with a stream of  $\text{CO}_2$  or  $\text{N}_2$ . This technique would appear simpler to implement from a sample handling viewpoint.

Another titration technique which appears reasonably direct is the titration of manganese(II) with permanganate in a near neutral pyrophosphate solution (12). In this titration Fe(III) does not interfere. However, Fe(II) would be expected to interfere. If Fe(II) is stoichiometrically titrated with the permanganate under this condition, the sum of Mn and Fe(II) could be determined. If not, a preliminary oxidation would be required to eliminate this interference.

(d) Complexometric Titration. Although several direct complexometric titration methods have been suggested (13), only one appears to be sufficiently simple to be considered for automation. This involves the titration of Mn(II) by EDTA and masking the interference of iron by reducing to Fe(II) and complexing with cyanide as the ferrocyanide. However, a heating of the solution is required (14,15) for complexing the iron, as well as the desirability of back titration which makes this procedure rather unattractive.

(e) Colorimetric Methods. In general, colorimetric methods have the disadvantage that if any other colored species are present, a spectrophotometer is necessary to discriminate the different wavelengths. If species which absorb at the same wavelength or particulates are present, interference will be found. The most common colorimetric method involves oxidation of the manganese(II) ion to permanganate with a suitable oxidizing agent (i.e., persulfate, periodate, bismuthate, lead dioxide, etc.) and measuring the color



of the permanganate ion. The same problems apply here as in the oxidation step of the titrimetric method. The solution must be heated when most of the oxidizing agents are used (exception; bismuthate) or else there is a problem of separation of the excess of the (insoluble) oxidizing agent. This type of procedure, therefore, would tend to complicate the automated analysis. The most common oxidizing agent is periodate (16). However, ferric ions are also said to slow down the oxidation (17), and ferrous ions will be oxidized before the oxidation with periodate.

Another colorimetric procedure which has been studied by several workers involves the reaction with formaldoxime. However, iron interferes and the masking of the iron is not straightforward (18). Other colorimetric procedures involve the Mn(III) ion in sulfuric acid, the Mn(III) diethyl dichrocarbonate complex and the green Mn(III) complex in basic triethanolamine (12), but the methods are considered of less practical importance, and have not been studied thoroughly. In addition, interference of iron is a general problem.

## 5. Zinc Ion

(a) Ion Selective Electrode. As described in the previous subsection on manganese, the possibility of using a selective ion electrode is attractive. There is not an electrode which is specific to zinc, but there is a commercially available electrode which is highly selective to divalent cations. These two are the only divalent cations of any consequence in the bath. The selectivity coefficient for ferrous and zinc ions is reported to be identical (3.5 to 1) (9). The electrode response is, therefore, the same for both ions, and zinc ion can be used for calibration. The same variables as discussed previously need to be considered; namely, possible ionic strength changes in the bath, electrode reproducibility and stability, both short and long term (which dictates uncertainty in the measured metal ion concentration), and the effect of hydrogen ion and phosphate ion. If the sum of zinc and ferrous ions can thus be determined, (ferrous ion concentration can be determined separately by titration as described earlier) zinc could then be obtained by difference. In this manner good precision would still be obtained for ferrous ion, the more important species for bath control, while the precision of the zinc analysis would be about that of the total divalent cations.

As discussed previously, another use of the divalent cation electrode is for the end point detection of a complexometric titration. In a later section the specific details of the analysis procedure will be examined.

(b) Polarographic Methods. As described in the manganese subsection, if the concentration of ferric ion in the bath is small enough to be ignored, either pulse or normal polarography could be used to monitor simultaneously both ferrous and zinc ions even if the wave for the iron couple is reversible. Pulse polarography has the advantage that it is less subject to interference (e.g., oxygen), to small changes in the drop time of the electrode, and to bath conditions (e.g., stirring); in addition, neither the solution at the electrode nor the electrode is changed as a result of the measurement. Thus, there is more chance of using a solid electrode with this technique.

Table 4 gives some possibilities for a suitable supporting electrolyte for the simultaneous determination of zinc and ferrous ions. All those listed which show possibility involve only the addition of a single reagent mixture, and requires no heating, or other sample handling to obtain concentration of both ions. This obviously has advantages for automation provided the concentration measurements can be made with sufficient precision.

(c) Titration Techniques. The classical and most commonly used technique for the determination of zinc involves the precipitation titration with ferrocyanide. This technique is currently being used for this analysis. The ferrous ion present in the original solution must be removed. This is currently done by careful titration to the stoichiometric end point with potassium permanganate. The interference of ferric ion can be eliminated by use of pyrophosphate ion, and manganous ion does not interfere.

If this technique were used in an automated scheme, either ferrous would have to be oxidized by stoichiometric titration, or through the use of an oxidizing agent. The use of ozone as suggested earlier, would seem to have many advantages. Modification of the presently used procedures to eliminate addition of solid reagents and heating of the solution would be highly desirable and would not appear too difficult. Either a potentiometric (19), amperometric (20), or dead stop end point (21) is preferable and would seem to be adaptable (Table 5). This titration cannot be recommended for an automated

Table 4. Possible Electrolytes for Simultaneous Determination of Zinc and Ferrous Ions\*

Electrolyte	Electrode Reaction	$E_{1/2}$	Suggested Technique	Suggested Procedure
2F $K_2CO_3$ pH $\sim$ 11	$Fe(III) \rightarrow Fe(II)$	-0.53	Pulse Polarography.	Measure $Fe(II) \rightarrow Fe(III)$ at -0.25 &
	$Fe(III) \rightarrow Fe(II)$	-0.86		$Zn(II) \rightarrow Zn^0$ at -1.50.
	$Zn(II) \rightarrow Zn^0$	-1.20		
0.1F $(NH_4)_3$ Citrate pH = 6.1	$Fe(II) \rightarrow Fe(III)$	-0.183	Normal Polarography.	Measure $Fe(II) \rightarrow Fe(III)$ at -0.10 &
	$Fe(III) \rightarrow Fe(II)$	-0.225		$Zn(II) \rightarrow Zn^0$ at -1.50.
	$Zn(II) \rightarrow Zn^0$			
0.25F $Na_2C_2O_4$ pH $\sim$ 3.5	$Fe(II) \rightleftharpoons Fe(III)(rev.)$	$\sim$ 0.2	Normal Polarography.	Measure $Fe(II) \rightarrow Fe(III)$ at -0.05 &
	$Zn(II) \rightleftharpoons Zn^0 (rev.)$			$Zn(II) \rightarrow Zn^0$ at -1.5.
0.25F $Na_2$ Tartrate	$Fe(III) \rightleftharpoons Fe(II)(rev.)$	-1.0	Normal Polarography.	Measure $Fe(II) \rightarrow Fe(III)$ at -0.50 &
	$Zn(II) \rightleftharpoons Zn^0 (rev.)$			$Zn(II) \rightarrow Zn^0$ at -1.70.

\*Taken from Meites, L., Polarographic Techniques, Interscience, New York, 2nd Edition, 1965, p. 623.

Table 5. Comparison of Methods for Determination of Zinc

Technique	Description of Method	Interference	Advantage	Disadvantage
1. Potentiometric	ppt titration with potassium ferrocyanide	Fe(II)	Current Method	Titration is empirical, needs tight standardization, has false end point.
2. Amperometric	Same as 1.	Fe(II)		Same as 1.
3. Dead Stop	Same as 1.	Fe(II)		Same as 1.
4. Indicator (potentiometric)	Complexometric Titration with EDTA.	Remove interference of Fe(III) by glycerol.		Need to oxidize iron (II).
		Remove interference of Fe(II) by ascorbic cyanide ion.		Need to heat solution.
5. Colorimetric	Use of Zincon reagent.	Iron interferes.		Interference.
	Use of Chrome Azurols.	Iron interferes.		Interference.
	Dithizone	Iron, etc.		Extraction desirable.
6. Polarographic	Normal or pulse polarography.	See Table 4.		
7. Selective Ion Electrode	Measure potential of ion selective electrode.	Determine sum of Fe(II) and Zn(II).		See text.



scheme with much enthusiasm. The method is empirical and the composition of the precipitate depends on temperature, concentration of reagent and reactant, addition rate, etc. (22). A false end point is also apparently common when both indicators and potentiometry are used. While the former problems might be overcome by suitably standardizing the procedure, the false end point would be difficult in an automated analysis.

Complexometric titration with ethylenediaminetetraacetic acid (EDTA) is also rather common for zinc. Ferric and ferrous ions however interfere. Ferric ion has been masked by glycerol (23). Ferrous ion can be masked with cyanide (24) but heat is required. However, cyanide is not recommended for use in an automated field analysis, and thus one is left with an oxidation, then masking. Moreover, end point detection schemes other than indicators have not been exploited to any extent, and most work has involved a back titration of excess EDTA.

(d) Colorimetric Techniques. The classical colorimetric technique for zinc involves the use of dithizone (25). Many interferences exist. Zincon has also been used for colorimetric determination of zinc (26), but iron interferes. Other lesser known reagents (27) have been used, but interferences are also a problem. In addition, with colorimetric techniques, rather high dilutions of the bath would be required to use colorimetric techniques and the attainment of the required precision in the analysis may be a problem.

#### C. Recommended Method of Analysis (Summary)

There are many factors which must be considered in designing an analysis system. Among these are accuracy, reproducibility, reliability, simplicity, maintenance, calibration, and cost of development. This section will describe an analysis scheme felt to be most suited to this application, selected from the previously discussed techniques. It hopefully will also indicate how and why certain techniques were selected when others seem just as satisfactory. Table 6 lists the methods of analysis in order of preference. Obviously, if any of the principal techniques prove unsatisfactory when tested in the laboratory, the alternative methods would be developed.

##### 1. Free and Total Acid

Since these variables are probably the most important, this problem was

approached first. The free acid could be determined to within several percent by a direct pH measurement. However, there is only one method to determine total acid and that is by titration with base. Therefore, this method was selected also for free acid due to the added precision of titration with potentiometric end point detection compared to a direct potentiometric measurement.

## 2. Ferrous Ion

Here also the most precise results can be obtained by titration with potentiometric end point detection. Dichromate or ceric(IV) are more suitable as a titrant than permanganate due to greater stability. The choice between dichromate and ceric(IV) cannot be made on paper, but will depend on which gives the better results in the laboratory.

## 3. Nitrate Ion

Subject to the results of additional laboratory tests (described earlier), the nitrate ion selective electrode seems to be the best method for nitrate. It is simple, fast, and requires only the electrode for equipment, since one of the other titration vessels can be used as the sample container. Should this method fail, the colorimetric method for nitrate appears to be the next best approach.

## 4. Manganese(II) and Zinc(II)

Considerable development and equipment costs would be saved if the same technique were used for both manganese and zinc. Because of increased simplicity in sample handling and measurement, the use of direct potential measurement using a divalent cation electrode to determine the sum of Mn and Fe or Zn and Fe should be investigated. A calibration procedure may have to be employed. However, if this measurement cannot be made with the required precision or if the electrode is too unstable, then a complexometric titration procedure seems very attractive. Costs are further minimized since the procedure is titrimetric using identically the same equipment as the analysis for acid and ferrous ion.

An aliquot of phosphate solution is titrated with a basic EDTA solution in a vessel containing a reference electrode (SCE) and two indicator electrodes (a Pt wire electrode and a divalent cation electrode). Initially, as titrant

Table 6. Recommended Methods of Analysis

	<u>Principal</u>	<u>Alternate 1</u>	<u>Alternate 2</u>
Free and Total Acid	Potentiometric Titration		
Nitrate	Direct Potentiometric	Colorimetric	
Ferrous	Redox Titration Ce(IV)	Redox Titration ( $\text{Cr}_2\text{O}_7^{=}$ )	Polarographic
Zinc	Direct Potentiometric	Complexometric Titration	Polarographic
Manganese	Direct Potentiometric	Complexometric Titration	Polarographic

is added, the ferric-EDTA complex will be formed ( $pK_{Fe(III)} = 25.1$ ). When all the ferric ions are complexed, the potential of the platinum electrode will change significantly. The Pt electrode is only required if a significant amount of ferric ion is present in the bath. As noted before, it is not anticipated that this will be true. As the titration continues the solution becomes more basic forming the complexation of ferrous and zinc or manganese (whichever is present). The complex formation constants are sufficiently close ( $pK_{Fe(II)} = 14.33$ ,  $pK_{Mn(II)} = 13.79$ ,  $pK_{Zn(II)} = 16.50$ ) so that no break point will be detected as the individual species are complexed in turn. However, when the end point for the sum of both species is reached, the potential of the divalent cation electrode will change significantly. Calculated titration curves for equal amounts of Fe(III), Fe(II) and Mn(II) are shown in Figure 10. The zinc or manganese concentration can then be calculated from the amount of titrant used from the first break point (Pt) to the end of the titration, minus the contribution due to ferrous ion when it was independently determined.

Serious interference could be caused by other divalent cations. These species would have to be at concentrations greater than 1% of the zinc or manganese. However, from available information concerning bath composition, the problem seems remote. If such a titration procedure does not prove to be satisfactory, then a polarographic procedure should be investigated.



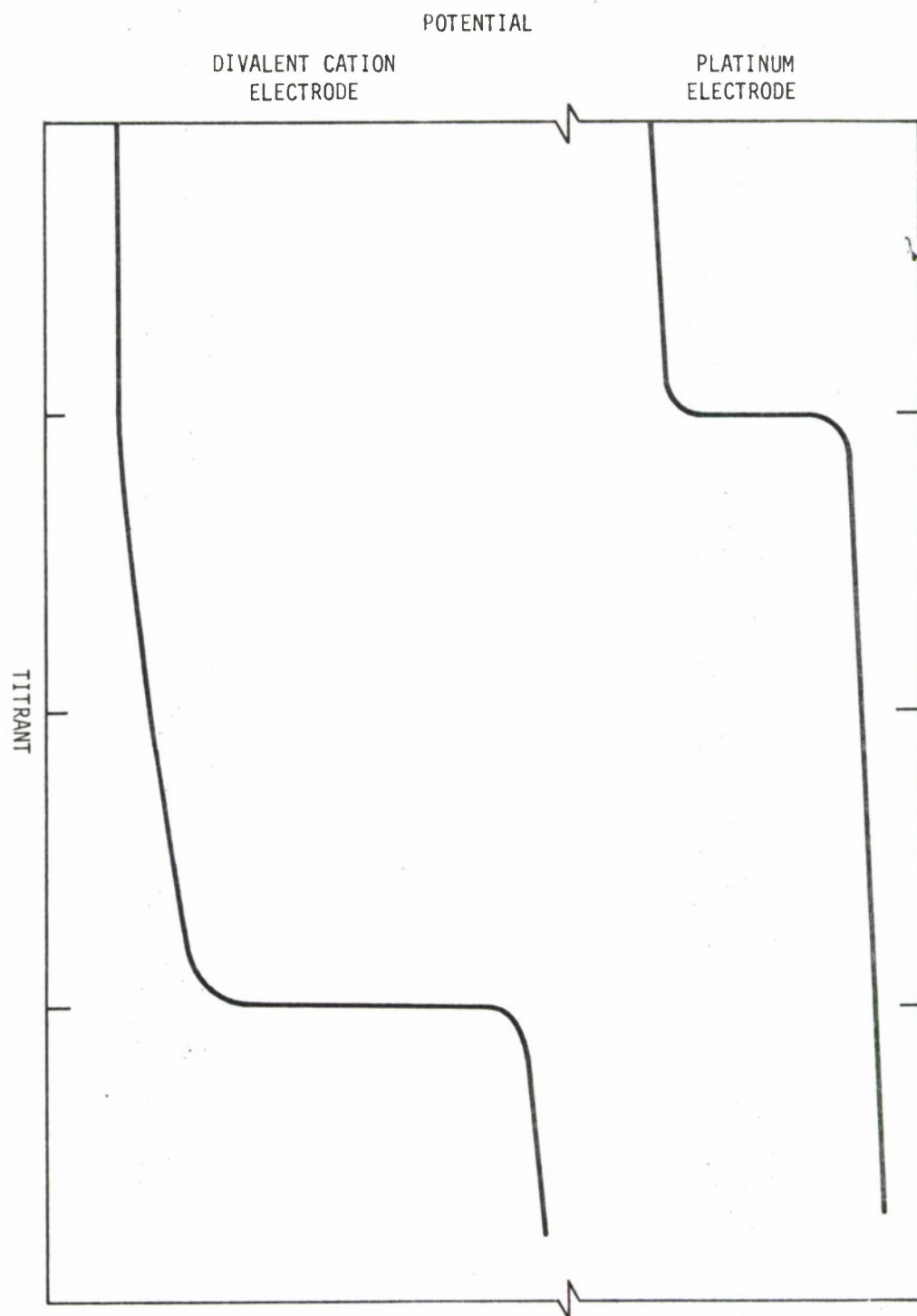


Figure 10 - Theoretical EDTA Titration Curve for Fe(III), Fe(II), and Mn(II)

## V. Sampling System

The function of the sampling system can be very simply stated. The sampling system must deliver a representative sample of accurately known volume to the analytical instruments. The key words in the previous sentence are "representative" and "known volume". The remainder of this section will discuss the problems associated with meeting those criteria.

### A. Obtaining a Representative Sample

The first prerequisite for obtaining a representative sample is that the bath composition is homogeneous. Recognizing that the sludge is not properly part of the specified analysis, homogeneous is meant to imply that the solution phase is for the most part in equilibrium. In fact, since particulates are especially detrimental to the reliable and accurate operation of precision sampling valves, it is quite probable that a filter will have to be installed at the intake to the sampling line to remove any particulate matter (sludge) suspended in solution. Studies by Gilbert have shown the processing of normal work introduces a local concentration gradient at or near the surface of the work (4). Thus, sampling near the work would produce biased results and should be avoided. A further aid to achieving homogeneity is stirring, a topic to be discussed in a later section.

Another difficulty in obtaining a representative sample is that of time fidelity. If an hour were required to obtain the sample, the results of the analysis would only be of marginal validity in terms of making decisions concerning corrective additions. To overcome this problem, a recirculating sampling line should be used. This would require a pump to circulate the solution through a pipe from the bath to the analytical instruments back to the bath. If a 1 cm (i.d.) pipe were used, the linear velocity in the pipe would be approximately 13 meters/min. per liter/min. of volume flow. Thus, if the instruments were 40 meters from the bath, the sample would arrive in 3 minutes, flowing at a rate of one liter/min. This would seem quite reasonable in comparison with the time response of the other bath parameters. The actual sampling valve would be located very close to the analytical instru-

ments to minimize the number of precision components necessary.

#### B. Precision Sampling Valves

An important criterion which should be used to select sampling valves is that of reproducibility. This satisfies the goal of delivering a known amount. It is not necessary that the sampling valve deliver 10.000 ml, but it is necessary that the valve deliver the same amount every time to better than 1%. The computer can easily correct for a sample size of 9.37 ml or 11.04 ml, as long as the amount is known and reproducible.

Sampling valves are available as standard items from several firms. Specific valves for this project should be chosen on the basis of: (a) delivery volume as required by the analysis scheme; (b) resistance to corrosion; and (c) reliability and wear resistance. For example, one manufacturer (Carle Instruments) markets a sampling valve which is particularly well suited to this application. The valve is constructed of tantalum, Teflon, and gold-plated stainless steel. The delivery volume, which can be from microliter to milliliter size, is reproducible to at least 0.1%. It could be argued that such a corrosion resistant valve would not be necessary for this system, but that stainless steel would be adequate. However, under certain conditions phosphoric acid will mildly attack stainless steel. This is not considered to be a severe problem for the switching valves, but for the sampling valves no corrosion is permissible.

#### C. Solution Multiplexing

The sampling system should be designed so that any one of several different sample lines can be selected. The important advantage of this approach is that one or more of the sample lines can be a calibration solution. The computer can then automatically check the calibration of the analytical instruments at regular time intervals. Another advantage of this approach is that the system is thus easily expandable to more than one bath. The main hazard of this design is the possibility of cross contamination of the solutions. This is not severe for the bath solutions, since the amounts involved are virtually negligible compared to the volume of the bath. However, calibration solution reservoirs would be much smaller and thus more susceptible to con-

tamination.

A simplified schematic diagram for a sampling system is shown in Figure 11. The stream selector valve (commercially available) connects one stream to the sampling line and returns the other streams to their respective sources. The sampling line passes through a series of precision sampling valves which deliver an aliquot of solution to the analysis vessels. Due to the possibility of solution contamination caused by the mixing of solutions in the sampling line, the exit of the sampling line is treated as waste.

#### D. Routine Tasks of the Sampling System

The sampling system must be capable of more than just obtaining the sample. An automated analysis requires also that the normal "housekeeping" functions of analysis must be performed. Included in this category are such tasks as: draining the analysis vessel, rinsing the analysis vessel, refilling the motor driven buret for the next titration, and other similar functions. As an example, an automated analysis of the free and total acid would involve the following sequence, which would be done by the computer through the sample handling system.

- (1) Add appropriate sample aliquot to cell.
- (2) Add water to dilute, if necessary.
- (3) Begin titration, adding base from motor driven buret and monitor pH.
- (4) Record volume of solution to predetermined pH for first end point.
- (5) Titrate to second end point and record volume to predetermined pH for second end point.
- (6) Dump contents of cell.
- (7) Rinse cell with water (or acid, if necessary) to remove precipitate and residual sample.
- (8) If acid is required to remove precipitate, rinse with water.
- (9) Refill buret from reagent storage.
- (10) Start again at (1).



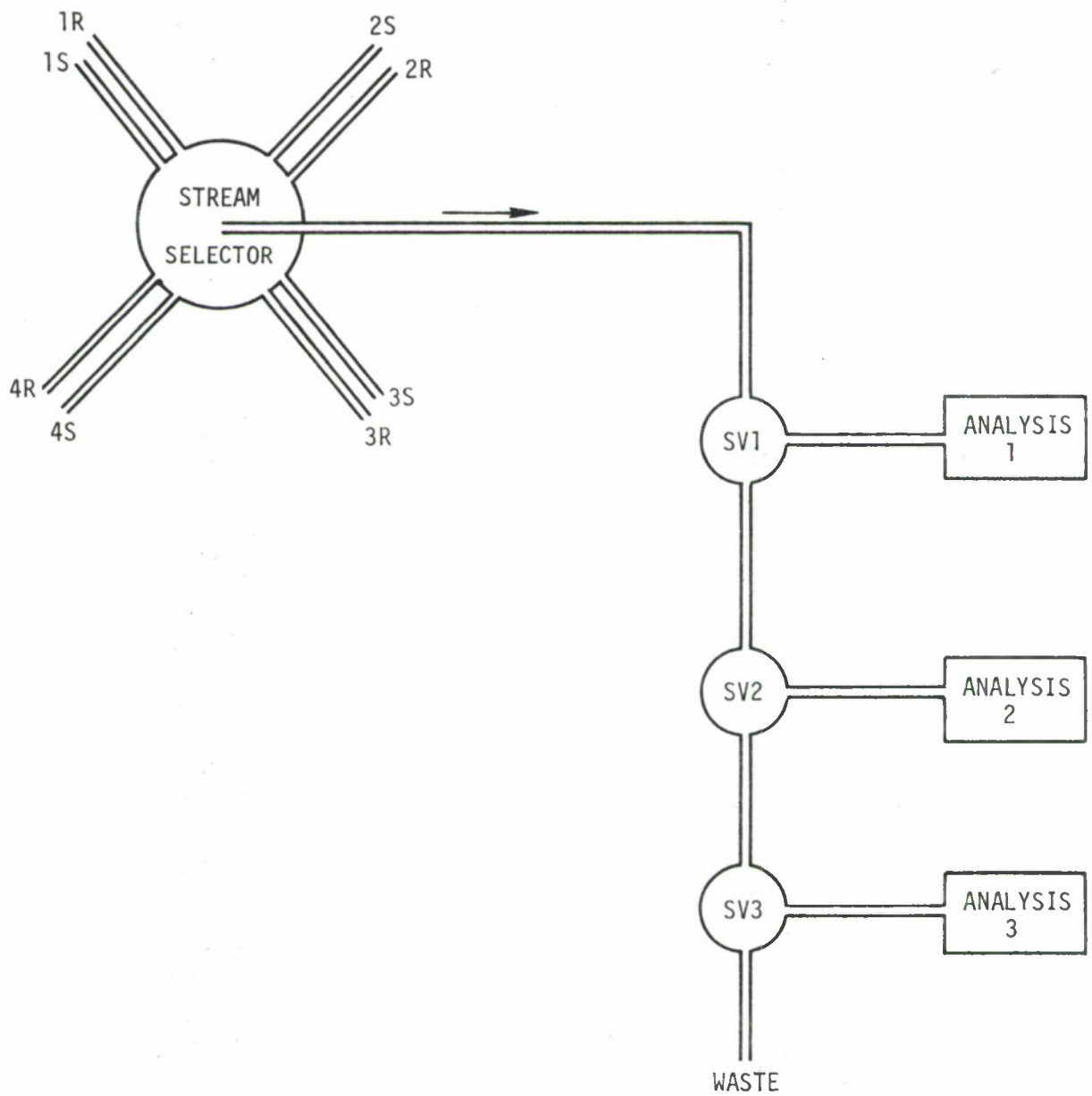


Figure 11 - Schematic Diagram of Liquid Sampling System

## VI. Control Strategy

The analysis and sampling systems have provided the computer with the concentrations of each of the important species. The next phase is to decide what action, if any, should be taken. This step is not as straightforward as it might appear and can be broken down into three separate problems. First, it must be determined if any species are outside acceptable limits. Second, if one or more species are not within the proper range, what reagent(s) should be added? Third, what is the optimum amount of the reagent(s) that should be added?

### A. Evaluation of Analytical Results

As the first step in the control process, the analytical results must be compared to the optimum values (Section II.B). This comparison must also include the error of analysis. Thus, the questions which actually must be asked are: "Is the measured value minus the analysis error less than the minimum and/or is the measured value plus the analysis error greater than the maximum limit?"

It is important to note that for all species there will be a concentration range including the analysis error which will be within the predefined limits. This establishes a deadband, i.e., there is no corrective addition necessary for this species. In this application, the deadband is quite valuable due to the problems associated with stirring after an addition (Section VII.A).

An important optimization will have to be made when defining the maximum and minimum concentration limits for each species. It is important to narrow the range since it is quite desirable that the bath never exceed the limits as delineated earlier (Section II.B). On the other hand, it is also important that the range be as wide as possible to minimize the number of additions to the bath. One of the important criteria which will be used as a basis for this optimization is a comparison between rate at which the bath composition changes and the rate at which composition errors can be detected and corrected. The relative time lags are also important since the stability of the control

loop is dependent upon their interaction.

#### B. Determination of Optimum Reagent(s)

Having determined that a particular species is out of range (preceding section), the optimum corrective reagent(s) must be selected. The most obvious approach would be to define a set of simultaneous equations which quantitatively describe the effect of addition of every reagent on the total bath composition. These equations could then be solved to arrive at an exact solution for any and all bath deficiencies. However, it is apparent from this study that the phosphating bath is sufficiently complex that all these relationships are not quantitatively understood and moreover are difficult to obtain. Therefore, another approach must be found.

The simpler and recommended approach is an iterative method. In this approach, the computer would be programmed to react in virtually the same manner as a human operator. For example, if the iron content is low, the operator would go to the manual (or more likely recall from previous experience) and determine that either Iron syrup should be added or that the solution should be artificially loaded, depending on the acid values being low or high. Thus, the computer could be programmed to go through the same type of decision making process. An example of a flowchart sequence for the decision making process is shown in Figure 12. This example is quite simplified and shows the decision process for only two cases. In the first case, all species (free acid, total acid, and Fe(II)) are within range and no control action is necessary. This is seen from descending vertically from START, through the OK response for each decision step and finishing at NO ACTION. In the second step, free acid is low and total acid and Fe(II) are satisfactory. The L branch from the first decision is taken, followed by the OK responses of the next two decisions, thus ending at ADD PHOSPHORIC ACID. Initially these responses would be based on previous results and the experience of current operators of the baths. However, during development work the computer program could be written so that poor decisions could be recognized and modified as control continues.

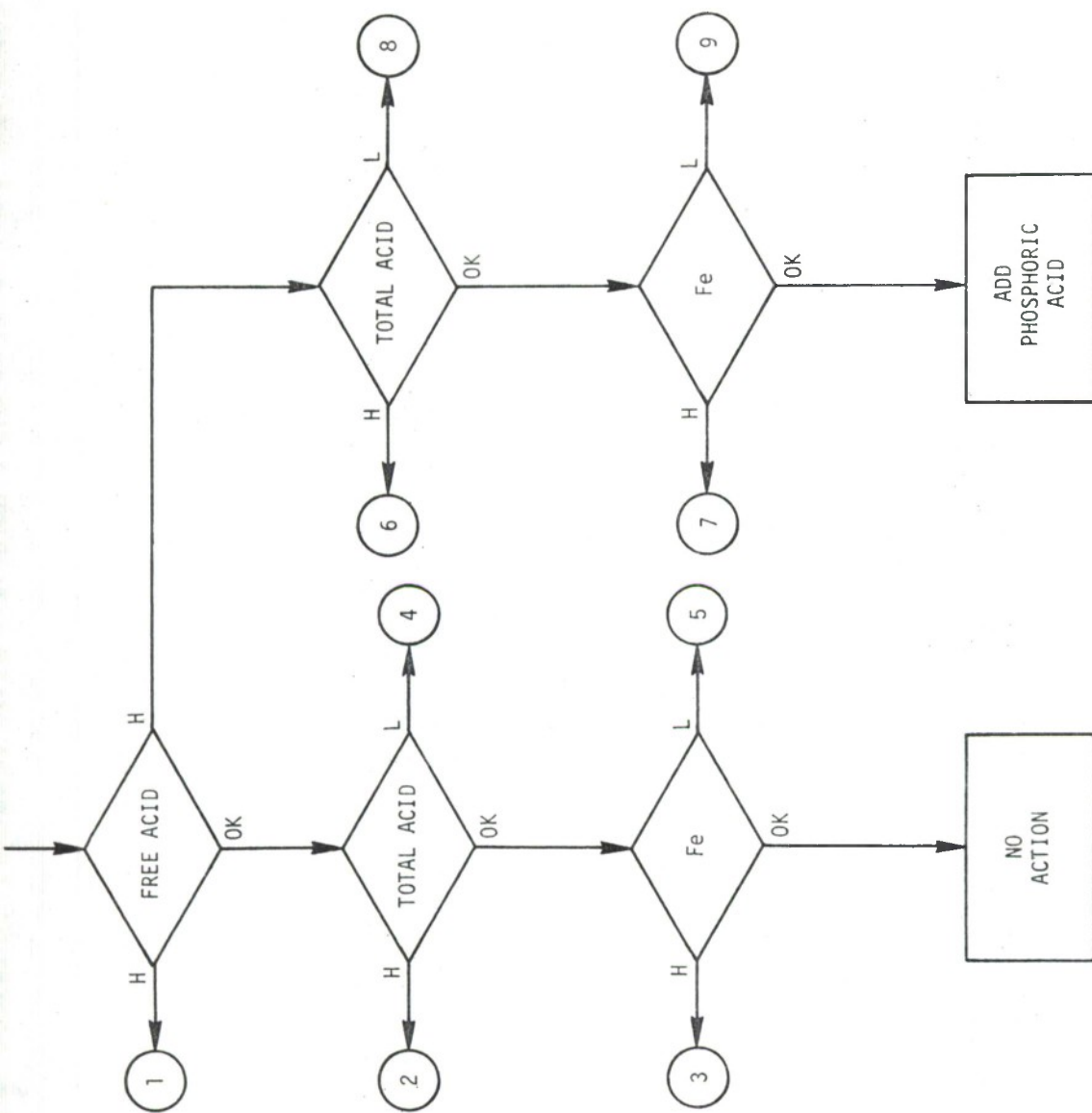


Figure 12 - Flow Chart of Decision Process for Reagent Addition



### C. Quantity of Reagent(s) Added

Sections V.A and V.B have discussed two aspects of the control strategy. The final aspect is that of determining the amount of reagent which is to be added. This element is equally as important as the first two, since the degree of control established over the bath is dependent on the amount added. If, for example, the proper strategy is selected, but the quantity is wrong, the concentrations will oscillate above and below the desired value if too much correction is made or will only slowly approach the proper concentration if the quantity added is too small.

Much of control theory has been devoted to the topic of loop gain and stability (28,29,30). Indeed if there were only one variable in the system, the problem of control would be very similar to that of the servo system of a recorder. In that case the pen is moved to a position which minimizes the difference between an internal potentiometer and the applied signal. If the gain of the servo system is too high, the pen oscillates. If the gain is too low the pen response is sluggish and does not quite follow the signal. Ideal response occurs when the gain is at an intermediate values ("critically damped"). This pattern is quite identical to that described for the phosphating bath. It is the purpose of this section to describe the basic elements of control with reference to how they will be used in this application. In no way will an exact procedure be specified. An approach will be given which specifies the starting point and indicates modifications which are available to overcome problems which may arise.

The error signal needed to activate the control strategy will, of course, be based on the results of the analysis. For the purpose of the following discussion, the error signal will be represented by  $\Delta C_t$ .  $\Delta C_t$  is derived from the difference between the measured concentration of a particular species ( $C_t$ ) and the optimum values for that species. For example, Fe(II) has an acceptable range of from 0.40 to 0.50% in the zinc phosphate solution. From this range the optimum value could be established as 0.45%. Based on these values,  $\Delta C_t$  for Fe(II) could be defined as

$$\begin{array}{ll} C_t - 0.45\% & \text{for } |C_t - 0.45| \geq 0.04\% \\ \text{and } 0 & \text{for } |C_t - 0.45| < 0.03\% \end{array}$$

This definition incorporates both the error of analysis (5% relative is equivalent to 0.09% absolute of 0.45%) and an anticipation factor such that an error signal is generated before the concentration exceeds the specified limits. The region where  $\Delta C_t$  equals zero is the deadband for this species.

With no a priori reason to suspect that the corrections to the bath will have to be rapid or that control stability will be critical, proportional control seems to be the best method with which to start. In this method the amount of correction is directly proportional to the error signal. Thus,

$$\Delta R_t = \alpha \Delta C_t \quad [3]$$

where  $\Delta R_t$  is amount to be added and  $\Delta C_t$  is the concentration error.<sup>†</sup>  $\alpha$  is a combination of several other constants and will include: conversion factors for units change as appropriate, volume of working solution, effectiveness coefficient (e.g., 1 pound changes concentration by 0.1%) based on existing knowledge, and an empirical weighting factor. The empirical weighting factor is an important parameter. It should first be set to unity and then modified to reflect the relative success or failure of previously applied corrections.

Should the proportional method of control be too slow to respond, a derivative component can also be added to increase the response. Derivative control could be used alone, but suffers from the fact that long term drifts are not adequately corrected, since the correction is based on the difference between the last error signals. Using a combination of proportional and derivative control, the correction takes the form

$$\Delta R_t = \alpha \Delta C_t + \beta (\Delta C_t - \Delta C_{t-1}) \quad [4]$$

---

<sup>†</sup> Before proceeding further, two points should be made concerning this analysis and description. First, for simplicity the discussion will reference only one variable. The extension to more than one variable is possible, but is not necessary for illustration here. Second, due to the nature of chemical control,  $\Delta R_t$  will be assumed to be positive. This is quite permissible, since in reality the sign of  $\alpha$  will change if the reagent raises or lowers the concentration of the particular species under consideration.

where  $\Delta C_{t-1}$  refers to the error existing at the time of the previous analysis and  $\beta$  is the weighting coefficient for the derivative portion.  $\beta$  contains the same factors as  $\alpha$ , but its final value is found by increasing the value of the empirical factor from 0 to a value which optimizes response. Two points are worth mentioning. First, if the value of  $\beta$  is too large, wild fluctuation will occur in the bath. Second, the previously determined value of  $\alpha$  will probably have to be decreased to maintain stability.

The most general form of control is proportional, plus derivative, plus integral. This is expressed as

$$\Delta R_t = \alpha \Delta C_t + \beta (\Delta C_t - \Delta C_{t-1}) + \gamma \sum_{k=0}^k \Delta C_{t-k} \quad [5]$$

where  $\gamma$  is defined as  $\beta$  and  $k$  is the "reset" frequency and is determined empirically. The integral component corrects for changes in loading which might otherwise cause long term drifts of concentration which are uncorrectable by the other components.

The computer programs developed for the project should be constructed with form three; proportional, plus derivative, plus integral. At the beginning of the test period a best guess is made for  $\alpha$ ,  $\beta$ , and  $\gamma$ . As the experimental results become available, the values of the coefficients would be appropriately modified. This approach would be much more efficient than trying to add, say, an integral component at a later time.

Another problem which has not been considered here, but must be a part of the development work, is that of initial start of a bath. This may require a separate program, since the normal program for control will probably require that the bath concentrations are close to their working range.

## VII. Reagent Addition

The problem of reagent addition is a crucial one to the ultimate goal of continuous analysis and control of phosphating baths. Several factors complicate this section of the system immensely. One problem is stirring to achieve homogeneity of the baths and another is the physical form of the currently used correcting reagents.

### A. Stirring of the Bath

Regardless of the final form of reagent addition used, the problem of bath stirring will have to be solved. From available information (4,6), it appears that the poor phosphate coating produced by a stirred bath is not caused by the agitation. Indeed this is what is expected after observing the agitation caused by hydrogen evolution during the course of applying a good protective finish. The problem seems to be caused by the dispersion of sludge through the solution which becomes entrapped in the coating mechanism.

Irrespective of whether corrective reagents can be added while material is being processed or not, a baffle will have to be designed and added to the bath. Even if the reagent is added between processing, the sludge should not be dispersed because of the time required for resettling. The baffle must have the properties that: a) allow the sludge to settle to the bottom of the tank, and b) permit sufficient interaction between the solution and the sludge so that equilibrium or quasi-equilibrium is maintained. One possible solution to the problem is simply to mount a series of slats just above the bottom of the tank. The sludge could settle to the bottom and if the stirring propellor(s) were directed at approximately right angles to the slats, the dispersion of the sludge would be minimized.

The method of stirring (propellers, turbines, etc.) will have to be designed in conjunction with the design of the baffle. This is particularly important since the effectiveness of the baffle is dependent upon the direction and velocity of the solution which is moving around it.

### B. Addition of Reagents

Just as it was necessary to develop new methods of analysis which are



compatible with continuous automated analysis, it may also be necessary to modify the reagent addition scheme currently in use. For the majority of cases, the corrective reagents are compatible with automated control (6). However, there are several notable exceptions as described below.

The reagents which are easy to dispense are homogeneous liquids such as phosphoric acid, replenisher and manganese and zinc nitrate solutions. If the mechanical equipment (pump, pipes, and valves) is constructed of the proper material (e.g., stainless steel, Monel, etc.), it is a straightforward process to deliver a known amount of compound to the phosphating bath. The delivery can easily be controlled by solenoid valves actuated by the computer.

The main problems of reagent addition occur in the cases of slurries (e.g., manganese carbonate) and irregular solids (e.g., steel wool, sheet shot or scrap iron). In these cases the most cost effective approach is to develop suitable liquid substitutes rather than design additional equipment to handle the present reagent form. The development of suitable reagents will be greatly simplified through the use of the continuous automated analysis equipment developed as part of the program. The analysis will be available almost immediately after equilibrium has been established or before equilibrium, if that is appropriate.

According to current procedures, it is anticipated that the reagents will be at room temperature when added to the baths. The main advantages are that no cost is necessary to preheat the reagents and that many of the reagents (those with phosphates) have a higher solubility at room temperature. It also seems reasonable to assume that the relative volume of reagent added versus the total bath is small enough so that no substantial temperature gradient will occur.

A further advantage of an all liquid reagent addition scheme is that it is easily expanded. After the initial shakedown period when one bath is being controlled, the delivery system could be expanded to several more baths by adding suitable feeder pipes and solenoid valves. Additional major investments would thus be avoided.

## VIII. Miscellaneous Considerations

In addition to the major problems of automatic analysis and control of phosphating baths discussed in Sections III to VI, there are several other variables which also must be controlled.

### A. Temperature Control

Temperature control of the bath is very important. The best coatings are obtained if the bath is operated at temperatures over 200°F. However, if the temperature exceeds the boiling point of the solution, the composition balance of the solution is destroyed. Apparently, the changes which occur upon boiling are so great as to render the solution virtually useless. This necessitates removing much or all of the solution and adding fresh chemicals to restore the bath to satisfactory composition. This is expensive in terms of both materials and downtime.

It is, therefore, necessary to install or implement automatic temperature controllers on the bath. Since thermostats and Fenwal type temperature controllers are readily obtainable and have histories of proven performance; they would be the most economical and reliable method of temperature control. It is important that the data acquisition system include a thermocouple to monitor the temperature of the bath and provide a record of the bath temperature. An alarm could then be sounded if the temperature of the bath were outside the acceptable limits. The main point is that temperature control is more suitably achieved if the computer is not included in the loop, but merely monitors the performance of the controlling device.

### B. Solution Level Control

Current phosphating baths have not been provided with any form of solution level control. The operators have been relied on to add water to supplement rinse water in maintaining the solution level against constant evaporation losses. Furthermore, the phosphate baths do not have drain or overflow provisions. This presents an additional consideration for automatic control.

A level sensor will have to be included in the final configuration of the bath. Unlike temperature control, level control should involve the computer.

Several factors must be considered. A deadband should be included to allow for the volume change when work is immersed in the bath. A decision should be made to determine whether corrective reagent additions made will be sufficient to raise the level back to within limits or whether water should also be added.

It would be most feasible in the automation project to just add a level sensor to the bath. The sensor should provide a direct measure of level of the bath. A possible choice for the sensor would be a float connected to a slide wire potentiometer to give a voltage signal proportional to the liquid level. If the preliminary tests indicate that an overflow provision is necessary, it could be designed and implemented at that time.

## IX. Site Considerations

The environment of a typical phosphating installation as set up at Rock Island Arsenal, not unlike other process environments, is unsuitable from the point of view of process control instrumentation. The temperature range would be in excess of 100°F during the summer months and could probably drop to 50°F - 60°F during the cold winter months. Also, the area immediately surrounding the bath has a high humidity due to evaporation loss from the baths operating at 200°F. The ambient air could also contain corrosive vapors from phosphate baths, chromic acid baths, and pickling operations not to mention sandblasting and degreasing operations occurring nearby.

Needless to say, the analytical and process instrumentation should be located in a more controlled environment if optimum results are to be obtained. As instrumentation is currently envisioned, it would occupy very nearly the same amount of floor space as that currently provided for the analysis of the bath solutions. Some additional space would also be required for carboys containing the analytical reagents and waste materials. Several limitations do arise from this choice of location being approximately 75 feet from the baths. However, neither seems to present a great difficulty.

The first problem caused by the distance between the baths and analysis instruments is that of transporting the sample. Several solutions to the problem exist. The first solution is to run the sample lines to the control room in a stainless steel tube covered with an insulating material such as asbestos. This introduces a time delay equal to the length of tubing divided by the flow velocity. However, this would



not seem to be a problem since the composition of the bath is estimated to change over a longer period of time. If cooling of the sample during transportation presents a problem, the transport lines could be steam or electrically heated to maintain the temperature. The steam could be obtained from tapping into existing facilities. If necessary, return lines could also be heated in a similar fashion to avoid any gradients in the bath. However, in view of the relative quantities involved, this appears to be a very remote possibility.

The second problem caused by distance is that of the transmission of electrical signals. Typically, minicomputer manuals indicate that peripheral devices should be located within 25 or 50 feet of the computer. This restriction is not applicable here since it applies only to pulse type signals in which the rise time must be less than 100 nsec. The signals which would be required to go from the computer to the baths are d.c. levels or level changes which can have rise times on the order of msec or more. This is permissible since these transition times are small compared with the time required to actuate solenoid valves.

## X. Calibration and Maintenance

One of the main criteria for judging the performance of an automated control system is reliability. It is extremely important that the system be capable of operating for a reasonable period of time (week, month, etc.) without operator intervention. It is difficult to predict a priori the mean time between failure of various components. The best approach is to select the most reliable components when constructing the system.

The routine calibration of the analytical instruments should be done automatically and at specific intervals. Suitable calibration solutions could be made which would be stable and yet simulate, as close as possible, the actual phosphate solution conditions. These solutions would then be circulated through the sample line and analyzed identically to the unknown phosphate solutions. The results of the analysis would be used to update the normal data analysis program. In addition, if the standardization data showed drastic changes from previous results, the operator would be notified and/or an alarm would be activated.

Routine maintenance for the automated system would not require significant amounts of time or material. Typical maintenance tasks would, for example, include: a) restocking the solutions used for the chemical analysis and calibration; b) inspection of valves, pipes, and pumps for leakage and corrosion; and c) lubrication of pumps, fans, etc. as necessary. Also, if filters were required in the sampling and analysis system, they would also have to be inspected and changed at regular intervals. The computer and electronics will most likely be the most reliable components of the system. Maintenance, other than periodic recalibration, would not be required for these components except in the case of failure.

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## 13. ABSTRACT

The feasibility of automating production phosphate coating process baths has been studied under the guidance of the Research Directorate of the Weapons Laboratory at Rock Island. The study comprised a detailed examination of the analysis and control requirements. Continuous automated analysis and control of phosphate baths are feasible. Analytical methods, sampling system procedures, and control logic techniques are presented for incorporation into a prototype system. (U) (Parry, E.P. and Myers, R. L.)



14.

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